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Effects of Suppressant Chemicals Mixing and Temperature on the Dissolution of Potash Core Materials

by

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Department of Chemical Engineering
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Saskatchewan Potash Producers Association

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1. SUMMARY

Groundwater seepage into underground potash mines creates serious problems that have been the focus of our research activities for the last two years. This groundwater has a great potential for dissolving ions from the adjacent solid materials through which it flows. To help prevent this phenomenon, chemical "suppressants", can be injected into underground brines. These chemicals are supposed to make the fluid saturated or even supersaturated with the solid formation of the mine.

A preliminary study of various chemical suppressants was carried out.[1] This involved the addition of various inorganic and organic chemicals to KCl saturated water and brines. The effectiveness of suppressants were compared and it was discovered that the real precipitation problem is governed by complex phase behaviour. In our 1988 report[2] the phase behaviour of a few complex systems were investigated.

The purpose of the 1989 work was to find the best suppressants for actual mine groundwater and core materials from potash mines. The dissolution rate of three different core particles in mine groundwater was examined. Using results published in the open literature and our previous reports[1,2], the best suppressant chemicals were tested for their effectiveness in reducing core dissolution. These suppressants were KCl, $CaCl_2$, Na_2SO_4 and methanol. The weight loss of the particles in brine and brine+ suppressant was measured. The form of the rate reaction was investigated. KCl was the most effective suppressant, reducing the dissolution rate significantly.

Similar experiments were carried out at different temperatures of 15, 35 and 45°C and different mixing rates of 170, 260 and 350 RPM. At the high mixing rate, the significant dissolution of particles occurs within the first twenty minutes indicating that the diffusion of ions through the film layer plays a very

significant role in dissolution kinetics. High temperature was also found to play an important role in dissolution rates. At high temperatures, suppressant behavior in some cases became ineffective.

In another experiment (CSTR), brine was pumped past a vertical core face and the brine contents were measured as a function of time. The core was treated with brine + suppressant as well. Concentration of the ions present in the solution were measured with respect to time. Pictures of the cores were taken after each experiment. KCl and Na_2SO_4 showed the best suppressant behavior in this experiment. However, plugging of the flow was a major problem encountered. Additives such as glycerol were used in order to increase the drag force on the particles in the direction of flow. This was frequently effective in delaying the plugging process.

Further, the Harvie and Weare computer model at 25°C was acquired and tested for predicting precipitation effects at high ion concentrations in pure component system and brine samples. The program was found to be very suitable for high concentration brine samples that were tested. Their program for higher temperatures (0 - 250°C) is also acquired but not yet assembled on our computer.

2. INTRODUCTION

The groundwater which enters the Prairie Evaporite Formation contains multiple dissolved ions. The brine samples chosen for our analysis came from Central Canada Potash and its analysis is reported in Table 1. This pure brine is very effective in dissolving potassium chloride which is a major component of raw core material. It is well known from past studies such as Van't Hoff and his coworkers[3] and D'Ans[4] and others that water becomes unable to dissolve solid materials once it becomes saturated with respect to a specific ion (common ion effect) or when its nature is modified by reaction with another compound (salting out effect). Both principles have been employed in these experiments.

Table 1 : Concentration of the Ions in CCP Brine

Ions	Concentration (g/l)
HCO_3^-	0.028
SO_4^{2-}	0.542
Cl^-	187.052
Ca^{2+}	11.305
Mg^{2+}	3.564
K^+	4.742
Na^+	99.119

The rate of dissolution of potash core particles in groundwater is a function of several variables. According to Levenspiel[5], for reactions in homogeneous systems, the obvious variables are: temperature, pressure and composition. In heterogeneous systems more than one phase is involved, hence the problem becomes more complex. Material may have to move from phase to phase during reaction; hence the rate of mass transfer can become important. In this project, the effect of temperature, concentration and the rate of mixing on the rate of dissolution of potash particles were investigated and the kinetics of these processes were studied.

Suppressants were added to the brine to reduce the rate of dissolution of particles. These suppressants were KCl, $CaCl_2$, Na_2SO_4 and methanol. The effect of suppressants at different temperatures and mixing rates were also investigated.

Several solubility software packages such as WATEQ[6], GEOCHEM[7] and PHREEQE[8] were tested in our previous report[2]. These computer codes were not applicable to electrolyte solutions of high concentration. The Harvie and Weare[9] program was acquired and tested with experimental data. This code was found to be an extremely accurate software package for predicting multicomponent, high ionic strength solubilities at 25°C. The Weare group are developing another package for higher temperatures (from zero to 250°C). The package is acquired with two data files. However, it is not yet assembled on our computer.

3. THEORETICAL STUDIES

3.1 Computer Model Operation

Our previous works [1,2] indicate that WATEQ[6] and GEOCHEM[7] packages are not reliable for concentrated brine solutions. In this year's work, three software packages of PHREEQE[8], PHRQPITZ[10] and Harvie and Weare[9] were tested. The PHREEQE package is not suitable for calculation of geochemical reactions in brines.

PHRQPITZ is a Fortran 77 computer program that makes geochemical calculations in brines and other electrolyte solutions to high concentrations. PHRQPITZ has been adapted from the U.S. Geological survey geochemical simulation computer code PHREEQE, in which the aqueous model of PHREEQE has been replaced with the Pitzer virial coefficient approach.

PHRQPITZ is designed to run on a Prime 850 mini-computer. A machine readable listing of PHRQPITZ, associated data files and test cases was written on a 360K 5¼ inch floppy disk. The contents of this disk could be viewed on an IBM-compatible PC but would not run on the PC. These floppy disks were used to transport the code to our main frame computer. In this process, a few changes had to be made in the program in order to be compatible with our mainframe computer.

With these modifications, the program runs successfully and was tested with several brine samples. PHRQPITZ is a user-friendly system. There are, however, some difficulties in finding the use of the best option in its application. PH data is required in this program.

Harvie and Weare model is based upon the semi-empirical equations of Pitzer[11] and coworkers and is valid to high ionic strengths. The model utilizes an algorithm for rapidly identifying the coexisting phases and their composition at equilibrium. The parameters for the activity coefficient expressions were obtained from binary and ternary system solubility and osmotic data. One of us made a trip to the University of California, San Diego Campus, Department of Chemistry and learned their mathematical model for the prediction of mineral solubilities in waters from zero to high concentrations at 25°C. The program was copied to a magnetic tape and was transferred to the mainframe computer on the campus at the University of Saskatchewan. A few small changes were made in the program and compiled. The program runs successfully and data of pure

components and brine samples were tested with the model. The model is in substantially good agreement with the experimental data, far better than any other software we have found and tested.

Another trip was made to the University of San Diego, at the end of this project, to copy their newly developed program for high and low temperatures (0 - 250°C). Their high temperature program is developed and tested for two data series of $(CaHCO3)^+$, Ca^{2+}, K^+, Na^+, Cl^-, SO_4^{2-}, H_2O and Ca^{2+}, Na^+, Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-, $CA(HCO_3)^+$. The first data series lack carbonate and Mg^{2+} components and the second set lacks K^+ and Mg^{2+}. They are, however, developing a data series that will include Mg^{+2} as well (Ca^{2+}, Mg^{2+}, K^+, Na^+, CL^-, SO_4^{2-}).

The source code for high temperatures and the two available data series were copied on tape. These programs are neither compiled nor tested with any of our experimental data.

The 25°C program (called EQUIL) can now run on Apple Macintosh SE/30. They permitted us to get a copy of their program on diskette provided a fortran compiler Mactran plus be purchased before attempting to compile and run their program.

3.2 Kinetic Studies

In the static tests, core particles were added to the brine or mixture of brine and suppressant. The reactions involved are heterogeneous reactions because more than one phase is involved. The reactions may be represented by

$$A(\text{fluid}) + B(\text{solid}) \longrightarrow \text{product (fluid, solid or both)} \qquad (1)$$

Solid particles shrink in size during the reaction and a fine, flaking ash product is formed.

The selection of a model for the representation of data without too many mathematical complexities is the purpose of this section. For the noncatalytic reaction of particles with surrounding fluid, there are two simple idealized

models, the progressive - conversion model and the unreacted - core model[5]. In the first model, the size of the particles remain unchanged. In the second model, however, reactions occur first at the outer skin of the particle. The zone of reaction then moves into the solid and particles shrink in size. In our experiments, size of the particles are changing continuously till the equilibrium conditions are established. The second model, therefore, fits our experiments more accurately.

The unreacted core model[12] is based on five steps occurring in succession during the reaction.

Step 1 diffusion of liquid reactant A through the film surrounding the particle to the surface of the solid,

Step 2 penetration and diffusion of A through the blanket of ash to the surface of the unreacted core,

Step 3 reaction of liquidous reactant A with solid at the reaction surface,

Step 4 diffusion of liquidous products through the ash back to the exterior surface of the solid, and,

Step 5 diffusion of liquidous products through the liquid film back into the main body of fluid.

At times, some of these steps do not exist. For example, if the reaction is irreversible, steps 4 and 5 do not contribute any resistance to the reaction. The relative resistances of the different steps are varied from one system to another. We should, therefore, consider the step with the highest resistance to be the kinetic rate - controlling step. Figure 1 shows a reacting particle.

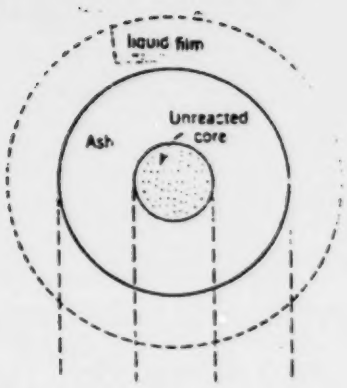


Figure 1 - Different Layers Present Around A Particle

For an irreversible reaction, either of steps 1, 2 and 3 could be rate-controlling. If the first step is rate-controlling, then we say that all of the resistance to mass transfer is found within a stagnant liquid film of thickness, S, next to a solid boundary. The concentration driving force is $C_{AL} - C_{AS}$. The reactant concentration at the surface is very low ($C_{AS} \approx 0$). Since the surface area of the particles are changing, based on the unchanging exterior surface of a particle, S, we can model this by:

$$-\frac{1}{S}\frac{dN_B}{dt} = -\frac{1}{4\pi R^2}\frac{dN_B}{dt} = -\frac{1}{4\pi R^2}\frac{dN_A}{dt} = -\frac{\rho_B r_c^2}{R^2}\frac{dr_c}{dt}$$

$$k_1 (C_{A1} - C_{As}) = k_1 C_{A1} = \text{const} \qquad (2)$$

where k_1 is the mass transfer coefficient between fluid and particle. After rearranging and integrating, we find how the unreacted core shrinks with time. Thus

$$\frac{t}{\tau} = 1 - \left(\frac{r_c}{R}\right)^3 = x_B \qquad (3)$$

where τ is the time for complete reaction of a particle, R is the radius of particles at time zero and r_c is the shrinking radius of the unreacted core.

If the diffusion through the ash layer controls the rate of reaction, then a few assumptions need to be made. First of all, the shrinkage of the unreacted

core is slower than the flow rate of A toward the unreacted core. Hence, it is reasonable to assume, that the unreacted core is stationary. This steady - state assumption allows simplifications in the mathematical calculations. The rate of reaction of A at any instant is given by its rate of diffusion to the reaction surface, or

$$-\frac{dN_A}{dt} = 4\pi R^2 Q_A = 4\pi R^2 Q_{AS} = 4\pi R^2 Q_{AC} = \text{constant} \qquad (4)$$

The flux of A within the ash layer can be expressed by Fick's law as follows

$$Q_A = D_e \frac{dC_A}{dr} \qquad (5)$$

where D_e is the effective diffusion coefficient of reactant A in the ash layer. Combining the two equations of 4 and 5 and after rearranging and integrating , we get

$$\frac{t}{\tau} = 1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^2 \qquad (6)$$

and in terms of fractional conversion, the equation becomes

$$\frac{t}{\tau} = 1 - 3\,(1 - x_B)^{2/3} + 2(1-x_B) \qquad (7)$$

where

$$1 - x_B = \frac{\text{volume of unreacted core}}{\text{total volume of particle}} \qquad (8)$$

Finally, if the chemical reaction is controlling, then the progress of the reaction is unaffected by the presence of ash layer. Based on a unit surface of unreacted core, the rate of reaction is

$$-\frac{1}{4\pi R_c^2}\frac{dN_B}{dt} = -\frac{1}{4\pi R_c^2}\frac{dN_A}{dt} = k_s C_{A1} \qquad (9)$$

where k_s is the first-order rate constant for surface reaction. Writing N_B in terms of shrinking radius, we obtain

$$-\frac{1}{4\pi r_c^2}\rho_B\, 4\pi R_c^2 \frac{dr_c}{dt} = -\rho_B \frac{dr_c}{dt} = k_s C_{A1} \qquad (10)$$

On integration, we get

$$\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_B)^{1/3} \qquad (11)$$

Usually there is no single resistance controlling the process throughout the experiment. The relative importance of each layer will vary as conversion progresses. For example, for constant size particles in the liquid, the ash layer resistance is nonexistent at the beginning because no ash is present, but becomes more and more important as the ash layer builds up.

The simultaneous action of these resistances is straightforward since they act in series. If they are linear in concentration such as a first order reaction then the individual resistances can be combined to give

$$-\frac{1}{S}\frac{dN_B}{dt} = \frac{C_A}{\frac{1}{kl} + \frac{R(R-r_c)}{r_c D_e} + \frac{R^2}{r_c^2 k_s}} \qquad (12)$$

The relative importance of the three individual resistances can now vary as conversion progresses.

The assumptions of this model may not match reality precisely. Despite this Wen[13] concludes that the shrinking core model is the best simple representation for the majority of reacting liquid-solid reactions. Figure 2 shows the progress of reaction with respect to time for different controlling steps.

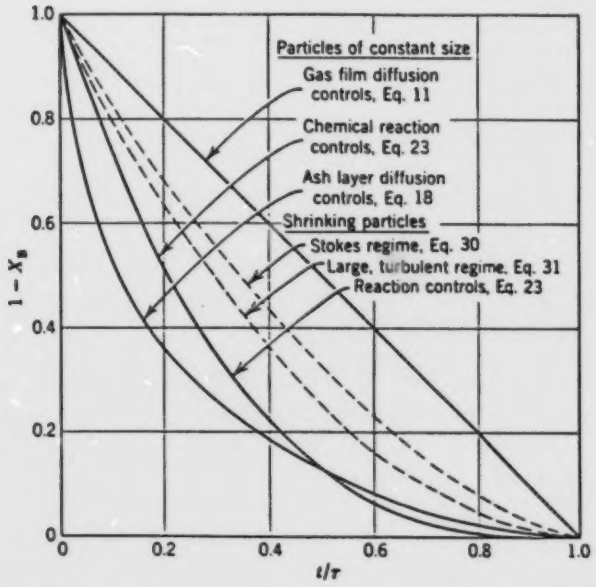


FIGURE 2 Progress of reaction of a single spherical particle with surrounding fluid measured in terms of time for complete conversion.

If the chemical reaction step is controlling, we may not have a first order irreversible reaction as discussed in the above example (simple case). To verify the rate of a chemical reaction, either theoretical considerations could be used or an empirical curve fitting test. In any case the value of the constants of the equation can only be found by experiment[5].

There are two procedures for analyzing experimental, kinetic data: the integral and the differential methods. In the integral method, we assume a particular form of rate equation and, after necessary integration and mathematical manipulations, the plot of a certain concentration function versus time should yield a straight line. If a reasonably good straight line is obtained, then the rate equation is said to satisfactorily fit the data. In the differential method of analysis, we test the fit of the rate expression to the data directly, and without any integration. Both methods have advantages and disadvantages. The integral method is easier to use and it is recommended for simple rate expressions. The differential method is useful in more complicated situations. In general, the integral analysis is attempted first, and, if not successful, then the differential method will be tried.

The data produced by the static test was analyzed by the Integral Method. In this method, a first order reversible reaction was tried for the determination of dissolution rate of core particles in brine plus suppressants. The reaction was assumed to be in the following form.

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} R \qquad K_c = \frac{K_1}{K_2} \tag{13}$$

and the dissolution rate can be written as:

$$-\frac{dC_A}{dt} = k_1 C_A - k_2 C_R \tag{14}$$

where: C_A = concentration of A

k_1 and k_2 = rate constant

C_R = concentration of product

and $C_R = C_{Ao} - C_A$

where: C_{Ao} = Initial concentration of A

we can, therefore, write

$$\frac{dC_A}{dt} = k_1 C_A - k_2 (C_{Ao} - C_A) \qquad (15)$$

Upon integration of the above equation, we get

$$\int_{C_{Ao}}^{C_A} \frac{kC_A}{(k_1 + k_2)C_A - k_2 C_{Ao}} = \int_0^t dt$$

Replacing,

$$U = (k_1 + k_2)\, C_A - k_2\, C_{Ao}$$

$$dU = (k_1 + k_2)\, dC_A$$

or

$$\int_{U_o}^{U} \frac{dU}{(k_1 + k_2)U} = \int_0^t dt$$

$$\int_{U_o}^{U} \frac{dU}{U} = \int_0^t (k_1 + k_2)dt$$

$$\ln U \Big|_{U_o}^{U} = (k_1 + k_2)\, t \Big|_0^t$$

$$\ln[(k_1 + k_2)C_A - k_2 C_{Ao}] - \ln (k_1 C_{Ao}) = (k_1 + k_2)t$$

$$-\frac{1}{k_1 + k_2} \ln \frac{k_1 C_{Ao}}{(k_1 + k_2)C_A - k_2 C_{Ao}} = t$$

or

$$-\frac{1}{k_1 + k_2} \ln \left[\left(1 + \frac{k_2}{k_1} \right) X - \frac{k_2}{k_1} \right] = t \qquad (16)$$

where: $X = \frac{C_A}{C_{Ao}}$ and

$$\frac{k_2}{k_1} = \frac{C_{Af}}{C_{Ao} - C_{Af}} \text{ at equilibrium} \qquad (17)$$

The plot of $\ln [(1 + k_2/K_1) X - k_2/k_1]$ versus time should yield a straight line which has a slope of $\frac{1}{k_1 + k_2}$. From the slope of the line which is $1/k_1 + k_2$ and the value of $C_{Af}/(C_{Ao} - C_{Af})$ which is equivalent to k_2/k_1, we would be able to calculate the rate constants of k_1 and k_2 for brine and also for brine and suppressants.

4. EXPERIMENTAL

Our experiments were grouped into these separate phases:

i) Static Tests

ii) CSTR Tests

iii) Plug Flow Tests

4.1 Static Tests

This test was carried out with brine samples from Central Canada Potash and three distinctive types of potash particles, two from CCP (called white and red hereafter, because of their colors) and one from IMC. The procedure was as follows:

- Potash ores were crushed at PCS pilot plant laboratory
- The particles were sieved to a required size range of (4.75 mm - 5.6 mm).

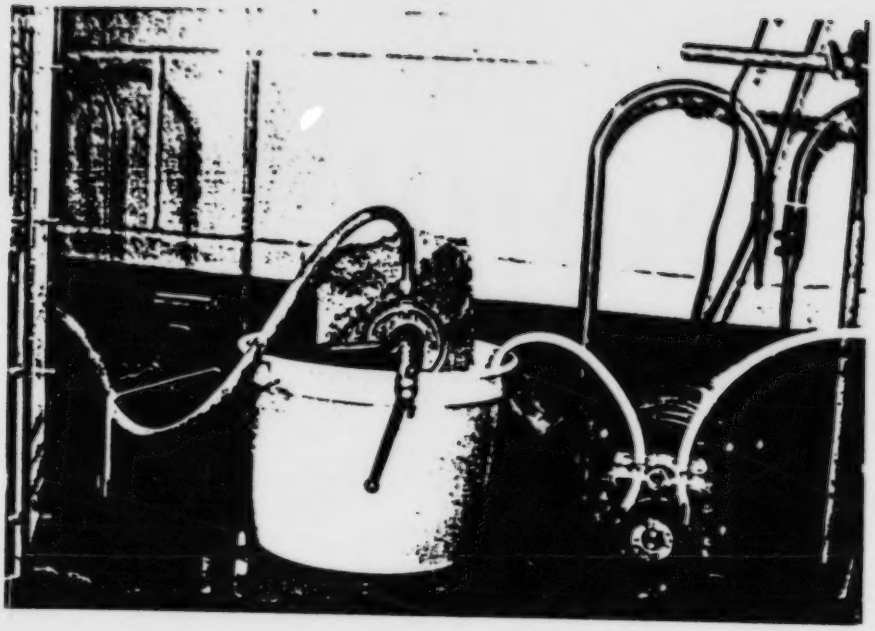
- 150 mL of CCP brine was added to a flask. The flask was placed in a water bath shaking machine for proper stirring at 25°C and 170 RPM.
- 30 gram of particles were added to the flask and were placed in the shaker at 25°C.
- The particles were separated from the solution by a filter and weighed at times 15, 30, 45, 75, 135, 195 and 255 minutes.
- Weight of the particles with respect to time were recorded.
- At the end of each experiment, the solution was filtered and liquid and solid phase samples were analyzed at the CCP laboratory (Appendix A).

Similar tests were carried out in the presence of different suppressants including $CaCl_2$, Na_2SO_4, KCl and methanol. Different amounts of suppressants were added to the brine such as 5, 10, 15 and 20 g of $CaCl_2$, 5, 10, and 20 g of Na_2SO_4, 5, 10 and 20 g of KCl and 25, 50 and 75 mL of methanol.

4.2 CSTR Tests

In this set of experiments, CCP brine and CCP ore lumps were used. Figure 3 shows the apparatus. The procedure was as follows:

- Potash ores were cut in small pieces with at least one surface area of 10 x 8 cm^2. The surface area had to be very smooth so that it is used as the contact surface. Core chunks were carefully cut and polished by technicians in the Geology Department on Campus.
- A small vessel, with an "O" Ring as the fluid sealant, was clamped to the surface of the core material and further sealed to the surface using silicone gasketing fluid.
- The brine was pumped past a vertical core by a calibrated pump from a well mixed holding tank.



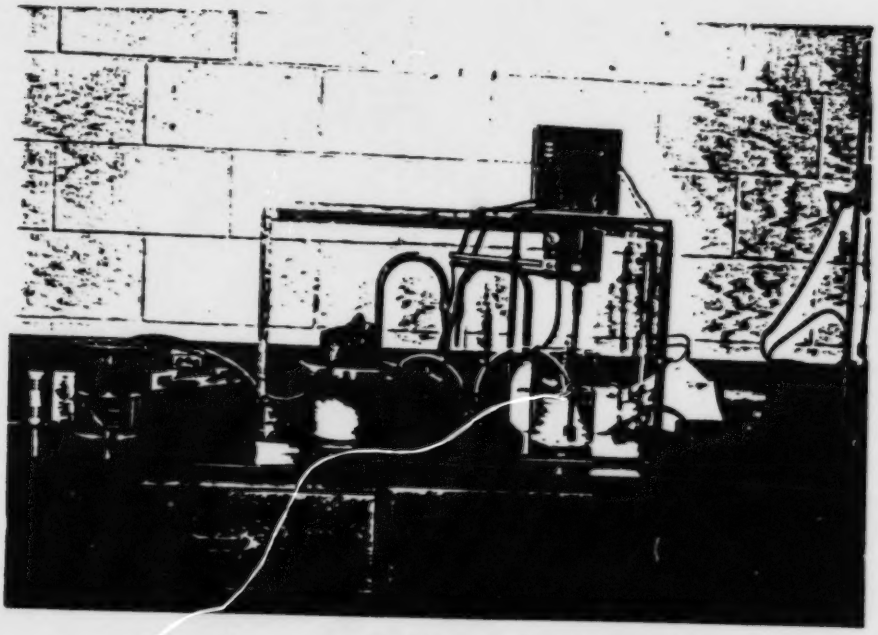


Figure 3 - Apparatus (CSTR Tests)

- The experiments were carried out in a temperature controlled, plexiglas chamber.
- The brine samples were collected every 15 or 30 minutes. Experiments ran between 2 to 8 hours.
- Samples were sent to CCP laboratory for analyses.
- Pictures of the core surface were taken after each experiment.

Two types of core materials were used and different suppressants were added to the brine. Suppressants were added for the purpose of reducing the rate of dissolution of brine. Some of these suppressants such as Na_2SO_4 formed a precipitate in the reacting vessel and soon plugged the flow of fluid. This problem was relieved by increasing the drag force on immersed objects. The drag force on an immersed object in the direction of velocity is controlled by the drag coefficient.

We need to increase the drag coefficient (C_D) for the purpose of increasing the drag force in the direction of velocity. Therefore we need to increase the velocity of the flow or the viscosity of the fluid or its density in order to increase the drag force on the particle. For a fixed velocity, we used additives such as glycerol so that the plugging rate could be reduced. Brine, therefore, was mixed with suppressants and additives before pumping past a vertical core. A few other additives were also tried. None of them, however, worked as well as glycerol. The theoretical background of drag force on the particle is available in Appendix A.

Circulation of the liquid inside the vessel was caused by injection of the fluid from the bottom of the vessel. The rate of fluid flow, therefore, controls the rate of mixing in the vessel. To get the highest rate of mixing, we simply had to increase the rate of fluid flow.

4.3 Plug Flow Tests

The design and construction of the apparatus was made. Experiments, however, could not be initiated because of the lack of potash cores from either IMC or CCP.

5. RESULTS AND DISCUSSION

5.1 Experimental

5.1a Static Test at 25°C and 170 RPM Mixing Speed

This set of experiment were carried out with CCP brine and 3 different core particles, two from CCP and one from IMC. The composition of CCP brine is shown in Table 1. Thirty grams of core particles (from each of the three different kinds) were dissolved in water and the solution was filtered. Tables 2 and 3 show the concentration of the saturated solution and composition of solid particles formed.

$CaCl_2$, KCl, Na_2SO_4 and methanol were added as suppressants to the brine. Figures 4, 5, 6 and 7 show the relative effects of different amounts of suppressants on the weight loss of CCP red particles and the data are tabulated in Table 4. Higher amounts of $CaCl_2$ such as 10, 20 and 30 grams yield similar effects (Figure 4). Figure 5 indicates that 20 g of KCl could completely stop the dissolution of particles in the brine. KCl therefore seems to be the best suppressant. Na_2SO_4 could also reduce the rate of dissolution, but its effect is not as significant as KCl. Different amounts of Na_2SO_4, however, could produce qualitatively similar results (Figure 6). Higher amounts of methanol had better effects on the rate of dissolution (Figure 7). Figure 8 compares the effect of some suppressants. The figure shows that suppressant in decreasing order of effectiveness are as follows:

20 g KCl > 20 g $CaCl_2$ > 125 ml MeoH > 20 g Na_2SO_4

Table 2 : Concentration of the Saturated Liquid Formed from Dissolution of 30 Grams of Core Particles in Water

Type	Density (g/l)	Concentration of Ions (g/l)						
		HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	K^+	Na^+
IMC	1.120	0.020	0.32	101.73	0.15	0.07	47.07	38.17
CCP white	1.127	0.025	0.03	108.82	0.01	0.03	23.46	56.76
CCP red	1.121	0.037	1.75	99.16	0.75	0.03	56.37	31.12

Table 3 : Composition of the Solid Precipitate Formed from Dissolution of 30 Grams of Core Particles in Water

Type	Weight Precent (%)				
	KCl	NaCl	$CaSO_4$	$MgSO_4$	$MgCl_2$
IMC	45.48	53.79	----	----	0.16
CCP white	28.16	71.86	----	----	----
CCP red	45.86	48.49	0.92	0.24	----

Figure 4 -

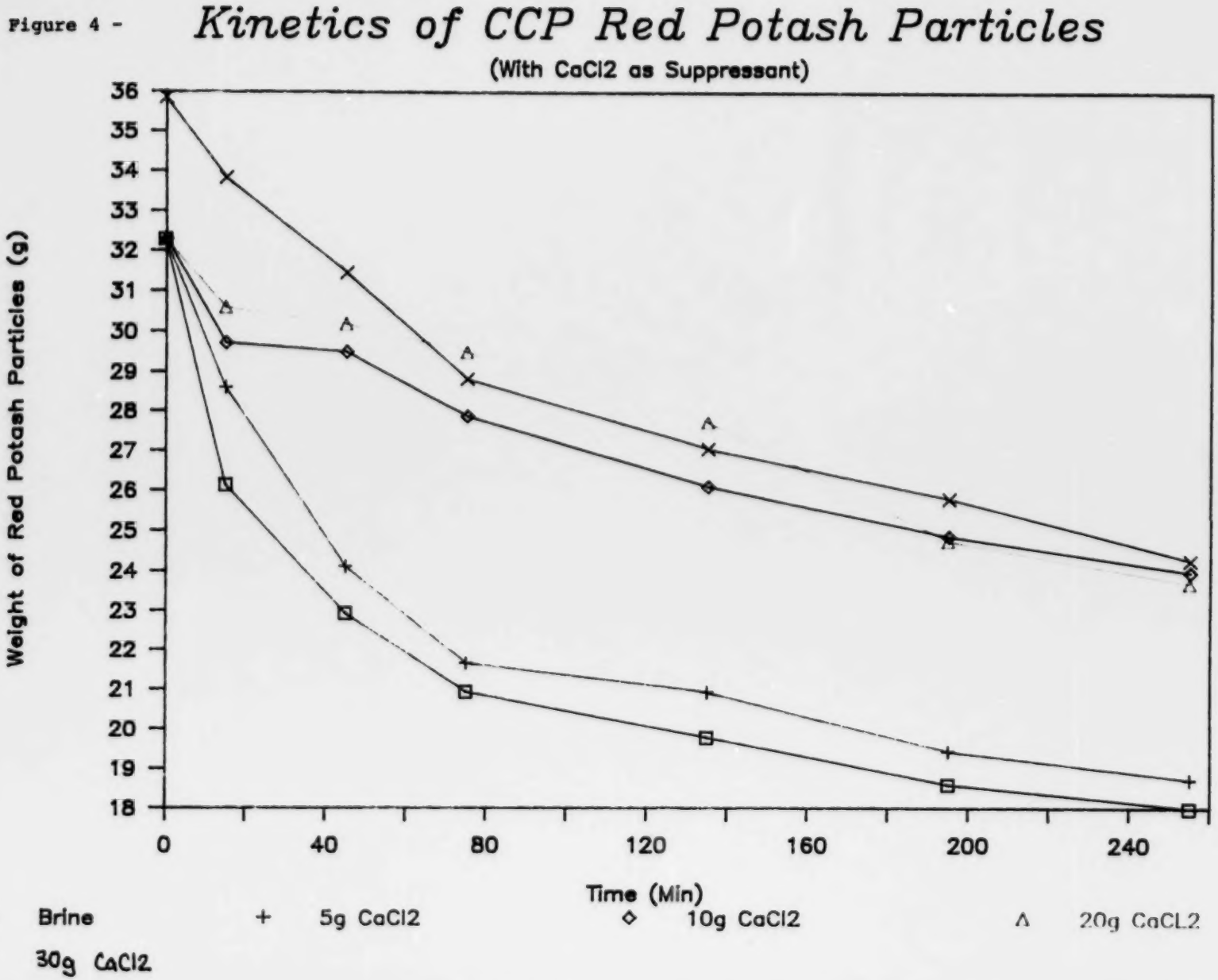

Kinetics of CCP Red Potash Particles
(With CaCl2 as Suppressant)
Weight of Red Potash Particles (g)
36
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
19
18
0
40
80
120
160
200
240
Time (Min)
Brine
5g CaCl2
10g CaCl2
20g CaCL2
30g CaCl2

Figure 5 - *Kinetics of CCP Red Potash Particles*

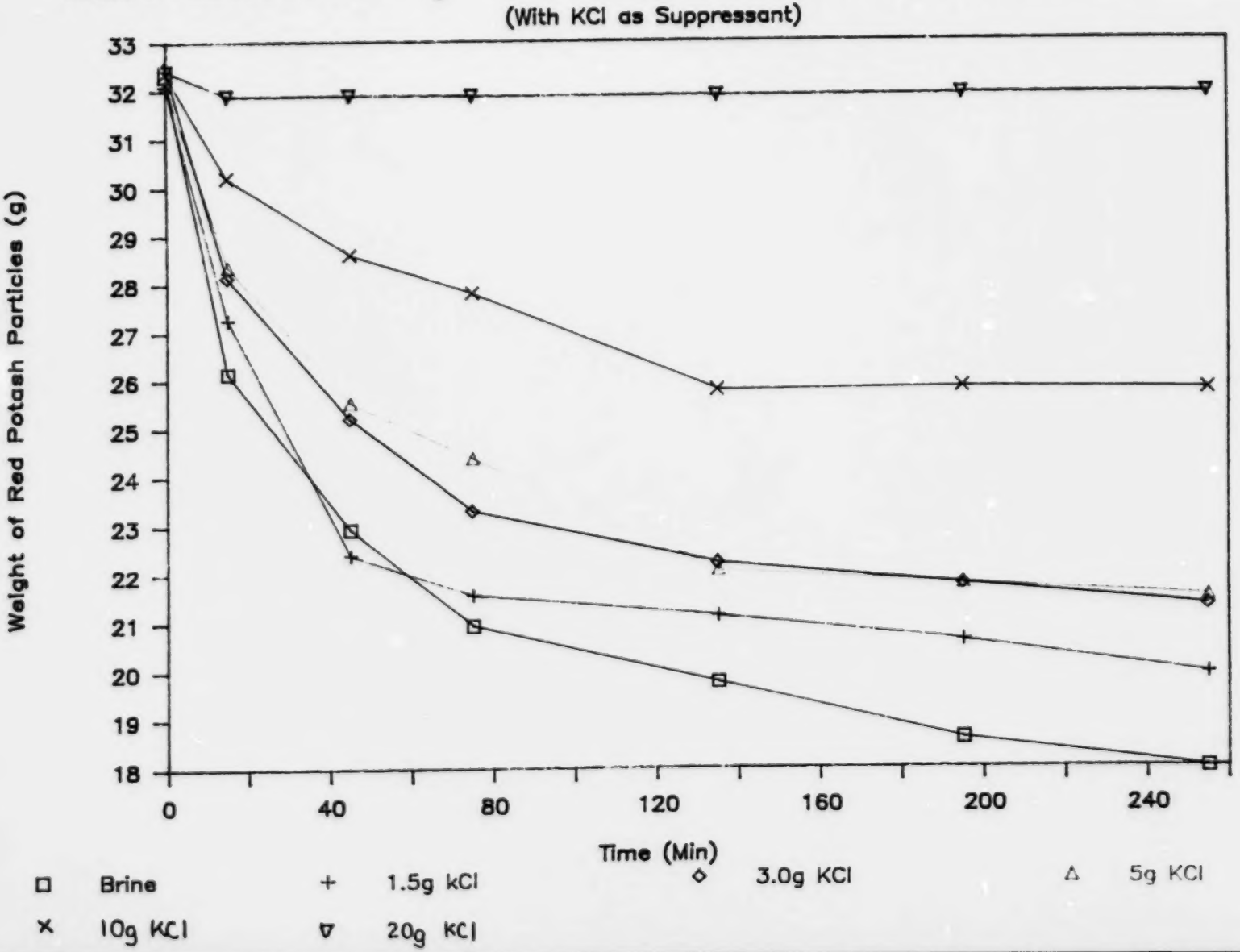


Figure 6 - *Kinetics of CCP Red Potash Particles*

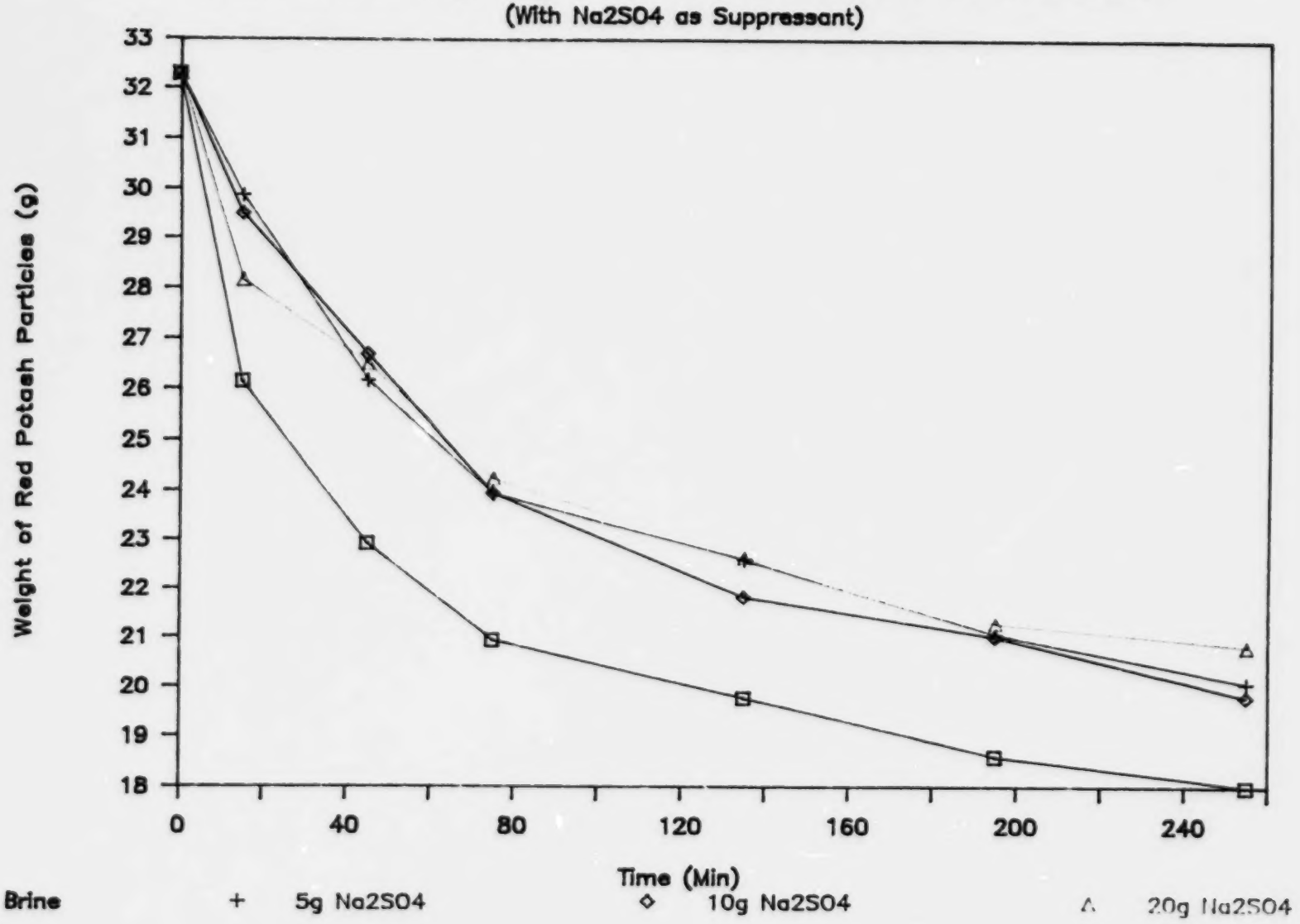


Figure 7 - *Kinetics of CCP Red Potash Particles*

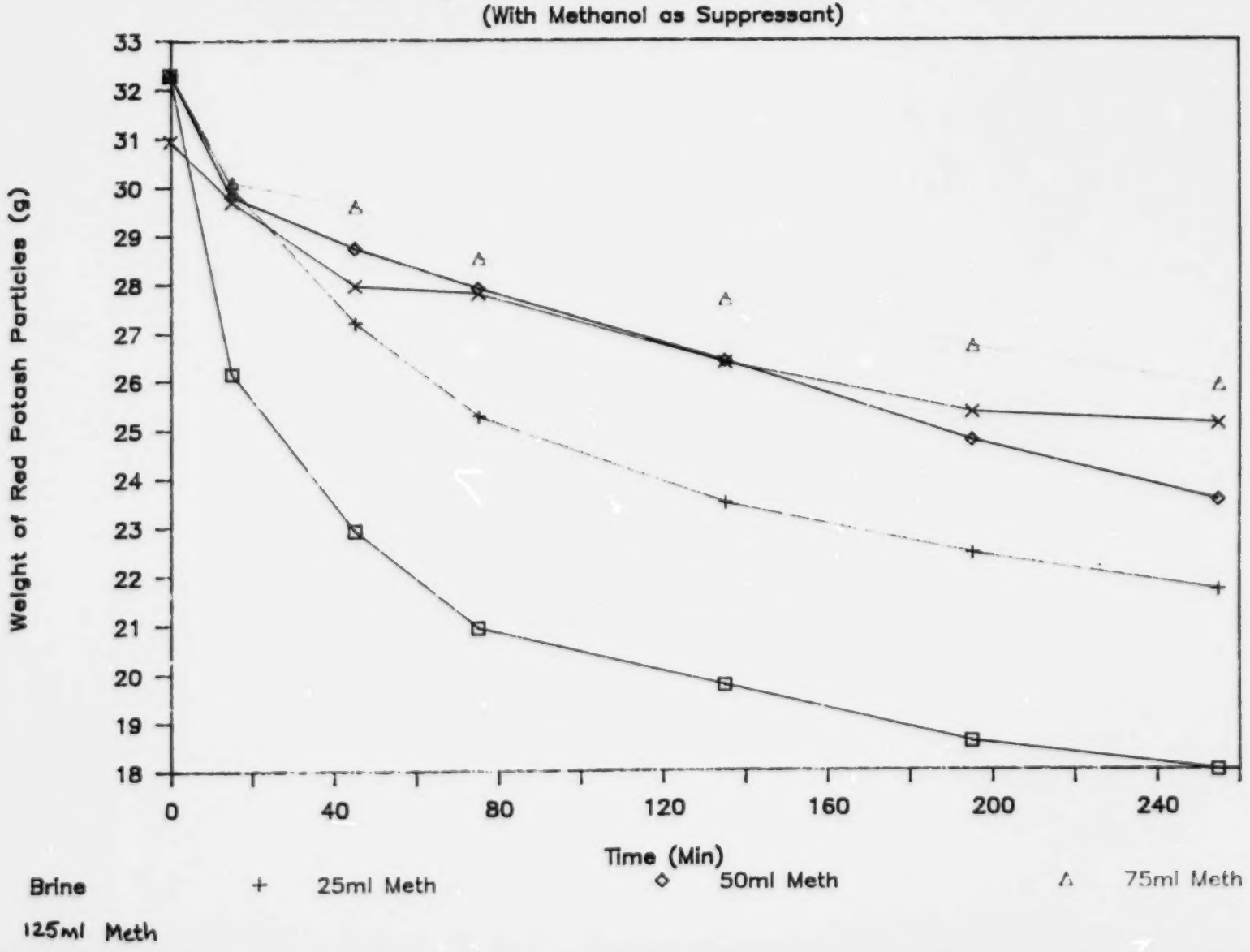


TABLE 4 - Kinetics of CCP Red Potash

With CaCl2 As Suppressant

Time (Min)	Weight of Potash Particles (g)				
	Brine	Brine + 5g CaCl2	Brine + 10g CaCl2	Brine + 20g CaCl2	Brine + 30g CaCl2
0.0	32.30	32.30	32.30	32.30	35.86
15.0	26.15	28.61	29.72	30.60	33.84
45.0	22.93	24.12	29.50	30.20	31.45
75.0	20.93	21.66	27.88	29.50	28.82
135.0	19.78	20.92	26.12	27.75	27.06
195.0	18.60	19.43	24.87	24.76	25.81
255.0	18.00	18.72	23.98	23.70	24.26

With Methanol As Suppressant

Time (Min)	Weight of Potash Particles (g)			
	Brine	Brine + 25ml Methanol	Brine + 50ml Methanol	Brine + 75ml Methanol
0.0	32.30	32.30	32.30	32.30
15.0	26.15	30.00	29.79	30.10
45.0	22.93	27.20	28.73	29.60
75.0	20.93	25.27	27.90	28.54
135.0	19.78	23.50	26.42	27.70
195.0	18.60	22.47	24.77	26.73
255.0	18.00	21.70	23.53	25.92

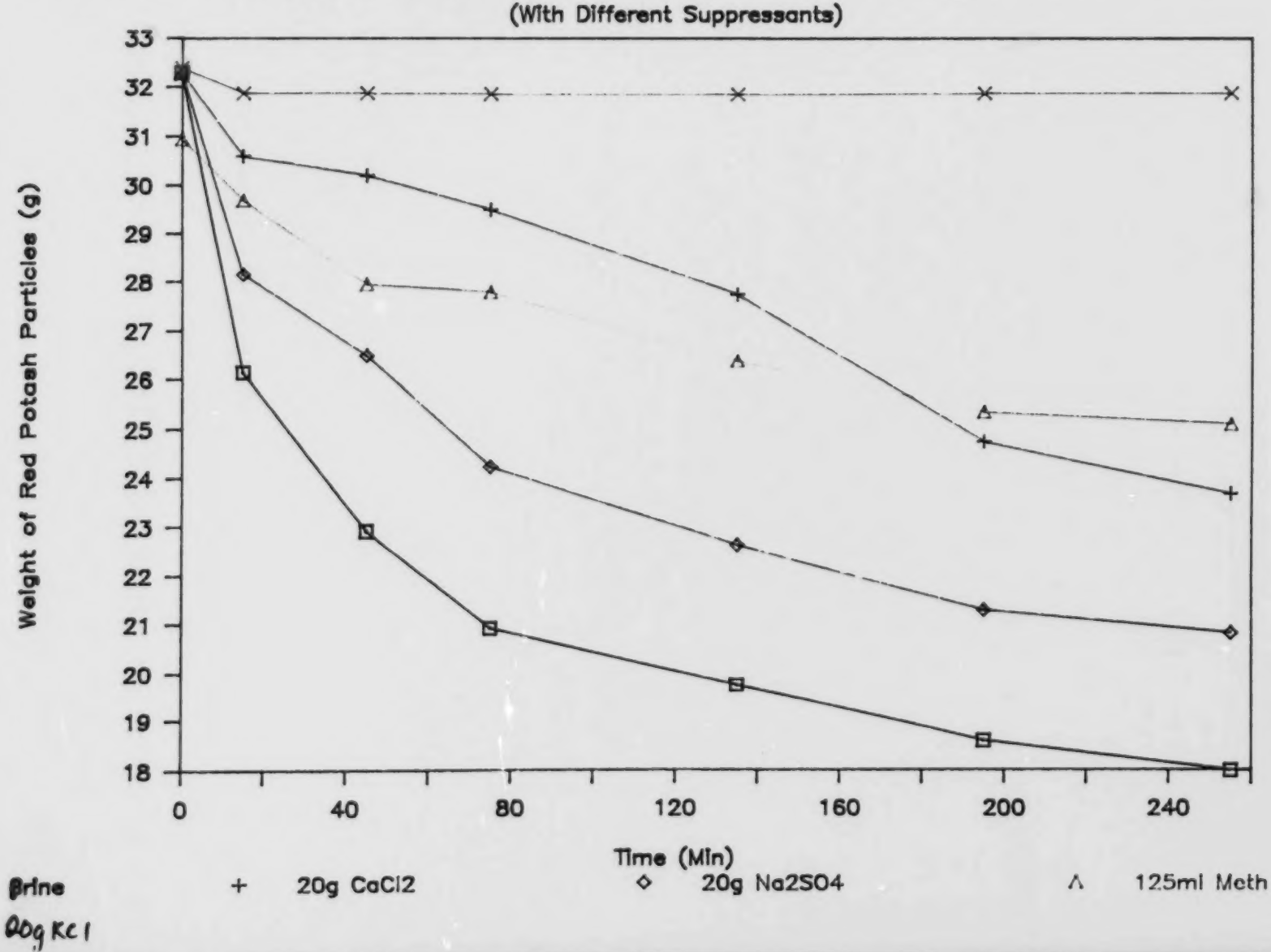
With Na2SO4 As Suppressant

Time (Min)	Weight of Potash Particles (g)			
	Brine	Brine + 5g Na2SO4	Brine + 10g Na2SO4	Brine + 20g Na2SO4
0.0	32.30	32.30	32.30	32.30
15.0	26.15	29.87	29.49	28.16
45.0	22.93	26.17	26.67	26.50
75.0	20.93	23.94	23.93	24.25
135.0	19.78	22.60	21.82	22.65
195.0	18.60	21.07	21.00	21.30
255.0	18.00	20.10	19.80	20.84

With KCl As Suppressant

Time (Min)	Weight of Potash Particles (g)					
	Brine	Brine + 1.5g KCl	Brine + 3g KCl	Brine + 5g KCl	Brine + 10g KCl	Brine + 20g KCl
0.0	32.30	32.10	32.48	32.13	32.36	32.40
15.0	26.15	27.27	28.15	28.38	30.21	31.88
45.0	22.93	22.41	25.21	25.55	28.62	31.88
75.0	20.93	21.57	23.31	24.40	27.82	31.86
135.0	19.78	21.14	22.25	22.10	25.80	31.85
195.0	18.60	20.62	21.79	21.81	25.85	31.88
255.0	18.00	19.95	21.34	21.53	25.80	31.89

Figure 8 - *Kinetics of CCP Red Potash Particles*



Static tests were carried out with CCP white potash particles and results are tabulated in Table 5 and shown in Figures 9, 10, 11 and 12. The higher the amount of suppressant the higher affect they could have on the rate of dissolution in any of these figures. KCl again seems to be the best suppressant (Figure 10). Figure 13 compares the effect of high amounts of suppressant on the rate of dissolution of CCP with particles. These suppressants in decreasing order of effectiveness are:

20 g KCl > 30 g $CaCl_2$ > 125 ml MeoH > 30 g Na_2SO_4

Static tests were carried out with IMC particles as well (Table 6). The composition of these particles are almost the average of the composition of CCP red and CCP white particles (Tables 2 and 3). Results for the brine and $CaCl_2$ are shown in Figure 14. Higher amounts of $CaCl_2$ yield better effects. 20 gram of KCl again could stop the dissolution of these particles in the brine completely (Figure 15). Na_2SO_4 was observed to have a little effect on the rate of dissolution (Figure 16). This is very similar to CCP red results (Figure 6). Methanol results are shown in Figure 17. The effect of high amount of suppressants are compared in Figure 18 and their effectiveness in decreasing order are:

20 g KCl > 30 g $CaCl_2$ > 125 ml MeoH > 30 g Na_2SO_4

We could, therefore, conclude that although the quantitative affect of suppressants on different potash particles vary, their effectiveness has similar order.

Some of these experiments were repeated so that the reproducibility of the results could be tested. Figures 19, 20 and 21 show the reproducibility of 3 suppressants for CCP red and Figures 22, 23 and 24 show the results for CCP white and the results of IMC potash particles are shown in Figures 25, 26, 27 and 28. These results are tabulated in Tables 7, 8 and 9. Most of these data points are

TABLE 5- Kinetics of CCP White Potash

With CaCl2 As Suppressant

Time (Min)	Weight of Potash Particles (g)					
	Brine	Brine + 5g CaCl2	Brine + 10g CaCl2	Brine + 15g CaCl2	Brine + 20g CaCl2	Brine + 30g CaCl2
0.0	32.60	32.60	32.60	32.60	32.60	33.45
15.0	28.91	29.96	30.00	30.40	30.87	33.03
45.0	25.72	28.67	29.85	30.24	30.69	33.09
75.0	24.05	27.75	27.60	29.70	29.93	33.02
135.0	23.60	26.70	26.20	28.86	28.51	32.99
195.0	23.10	26.50	26.00	27.70	28.00	31.89
255.0	22.70	26.40	26.10	26.84	27.55	30.39

With Methanol As Suppressant

Time (Min)	Weight of Potash Particles (g)				
	Brine	Brine + 25ml Meth	Brine + 50ml Meth	Brine + 75ml Meth	Brine + 125ml Meth
0.0	32.60	32.60	32.60	32.60	31.33
15.0	28.91	30.00	30.00	30.10	30.30
45.0	25.72	27.57	29.55	29.71	29.80
75.0	24.05	26.25	28.33	29.40	29.70
135.0	23.60	25.72	27.26	28.91	29.64
195.0	23.10	25.20	26.34	28.16	29.30
255.0	22.70	24.24	25.70	27.63	28.31

With Na2SO4 As Suppressant

Time (Min)	Weight of Potash Particles (g)				
	Brine	Brine + 5g Na2SO4	Brine + 10g Na2SO4	Brine + 20g Na2SO4	Brine + 30g Na2SO4
0.0	32.60	32.60	32.60	32.60	32.39
15.0	28.91	29.03	30.00	30.45	31.08
45.0	25.72	26.80	29.10	27.96	30.72
75.0	24.05	25.40	28.00	27.75	30.07
135.0	23.60	24.40	27.10	27.67	29.75
195.0	23.10	24.12	26.67	27.00	29.05
255.0	22.70	23.70	26.24	25.88	28.48

With KCl As Suppressant

Time (Min)	Weight of Potash Particles (g)			
	Brine	Brine + 5g KCl	Brine + 10g KCl	Brine + 20g KCl
0.0	32.60	31.97	32.13	32.59
15.0	28.91	29.08	31.15	32.56
45.0	25.72	28.04	29.57	32.41
75.0	24.05	26.88	28.94	32.50
135.0	23.60	26.20	28.62	32.49
195.0	23.10	25.59	28.40	32.47
255.0	22.70	25.53	27.78	32.51

Figure 9 - *Kinetics of CCP White Potash Particles*

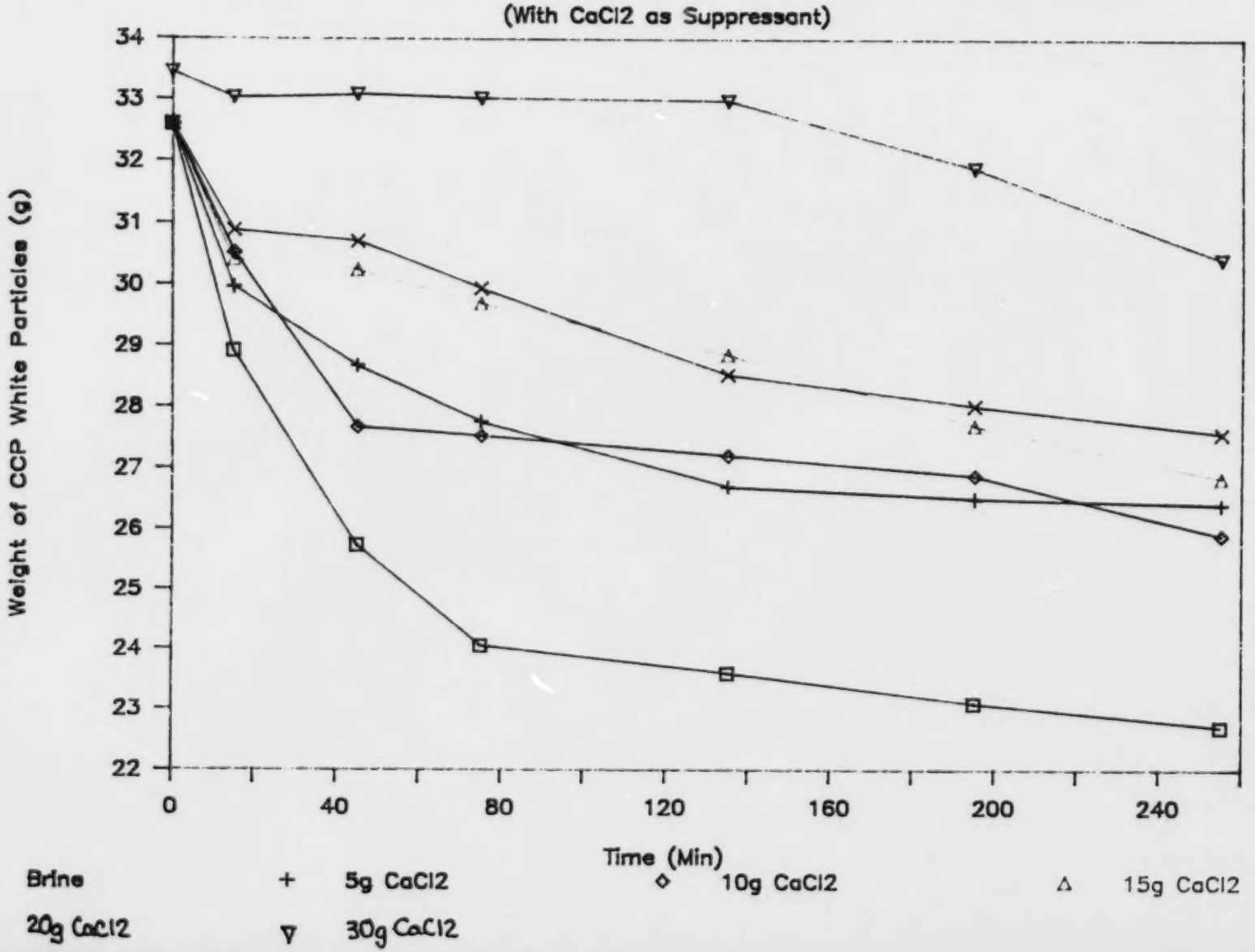


Figure 10 - *Kinetics of CCP White Potash Particles*

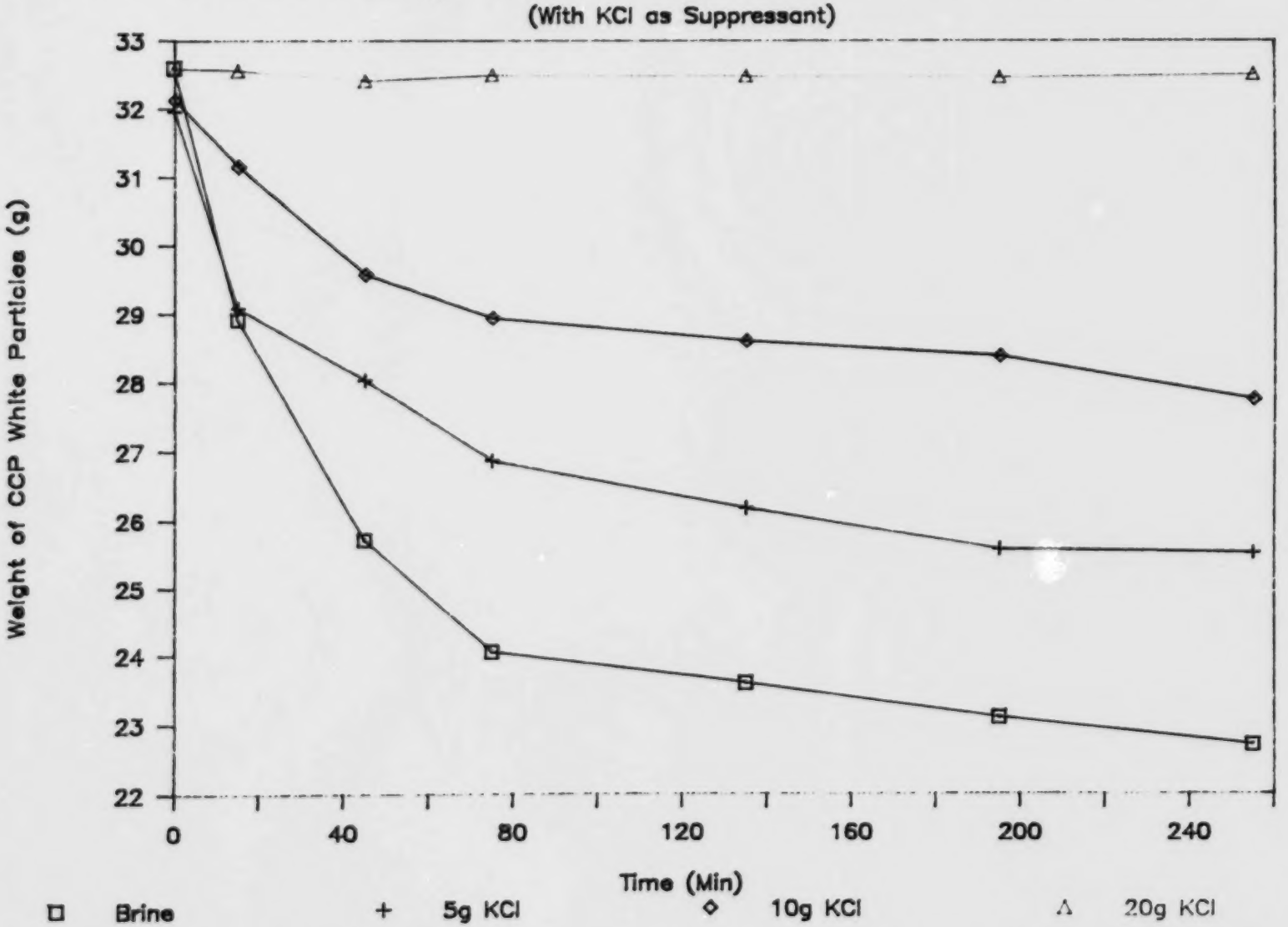


Figure 11 - *Kinetics of CCP White Potash Particles*

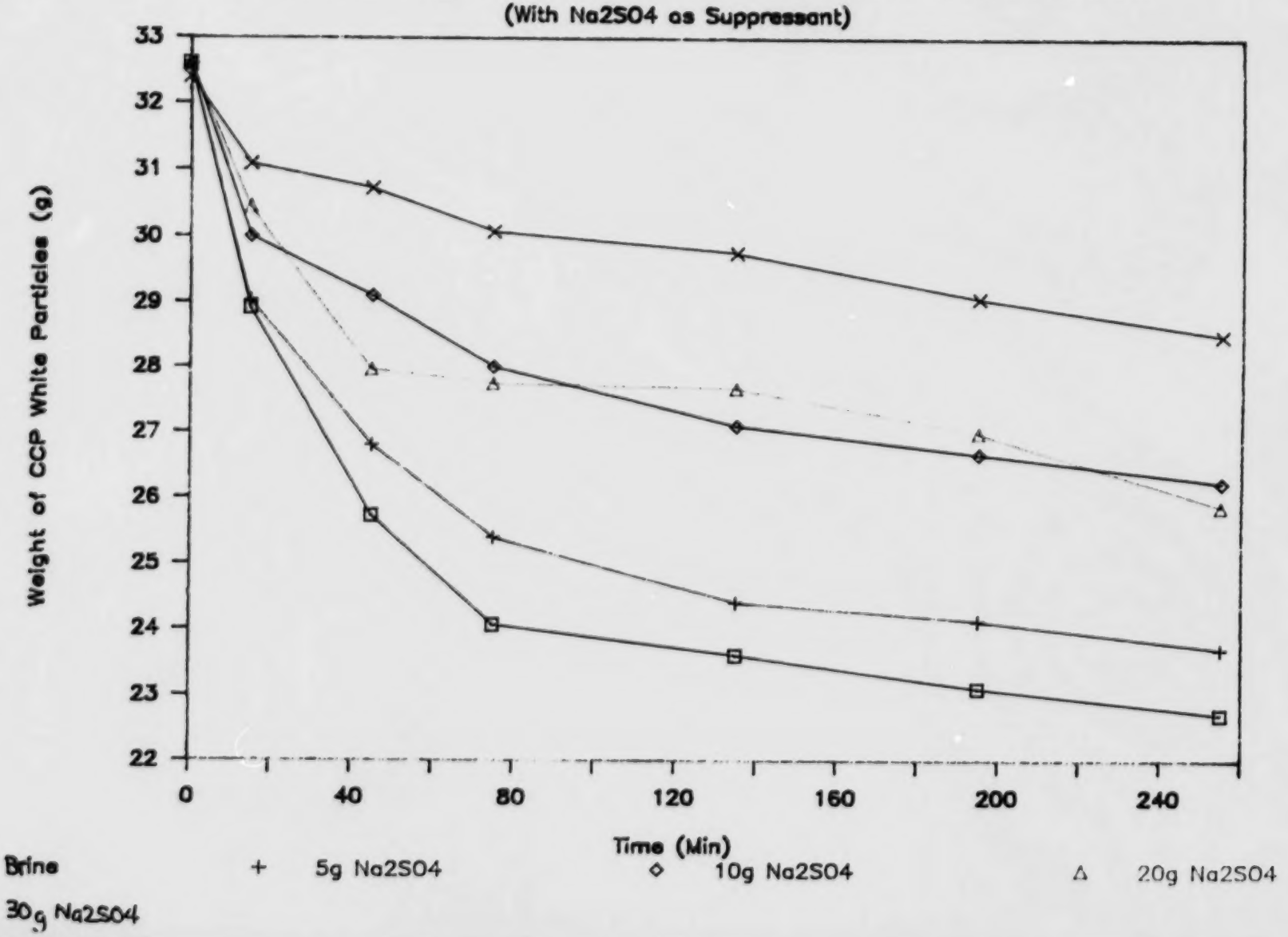


Figure 12 - *Kinetics of CCP White Potash Particles*

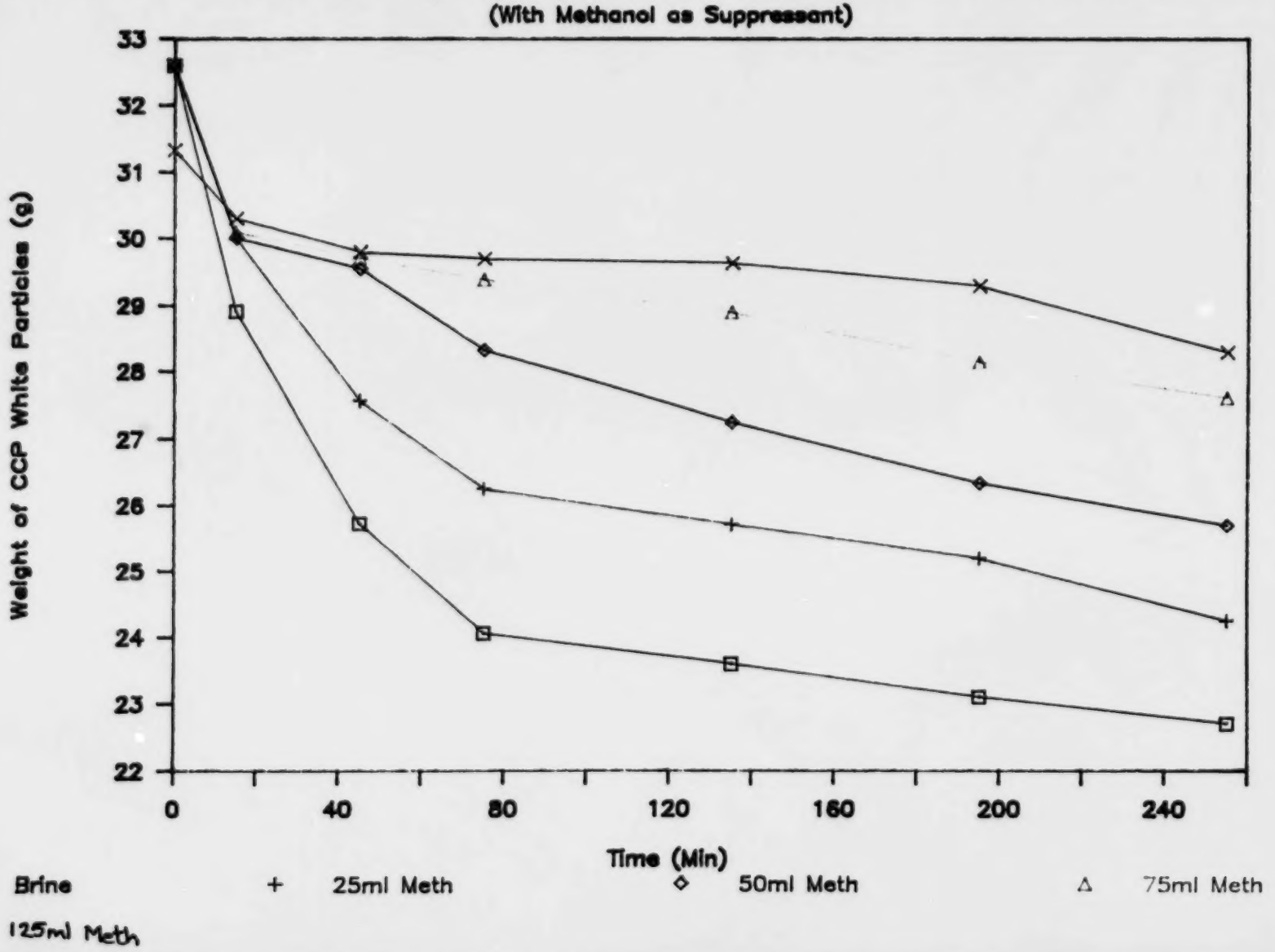


Figure 13 - *Kinetics of CCP White Potash Particles*

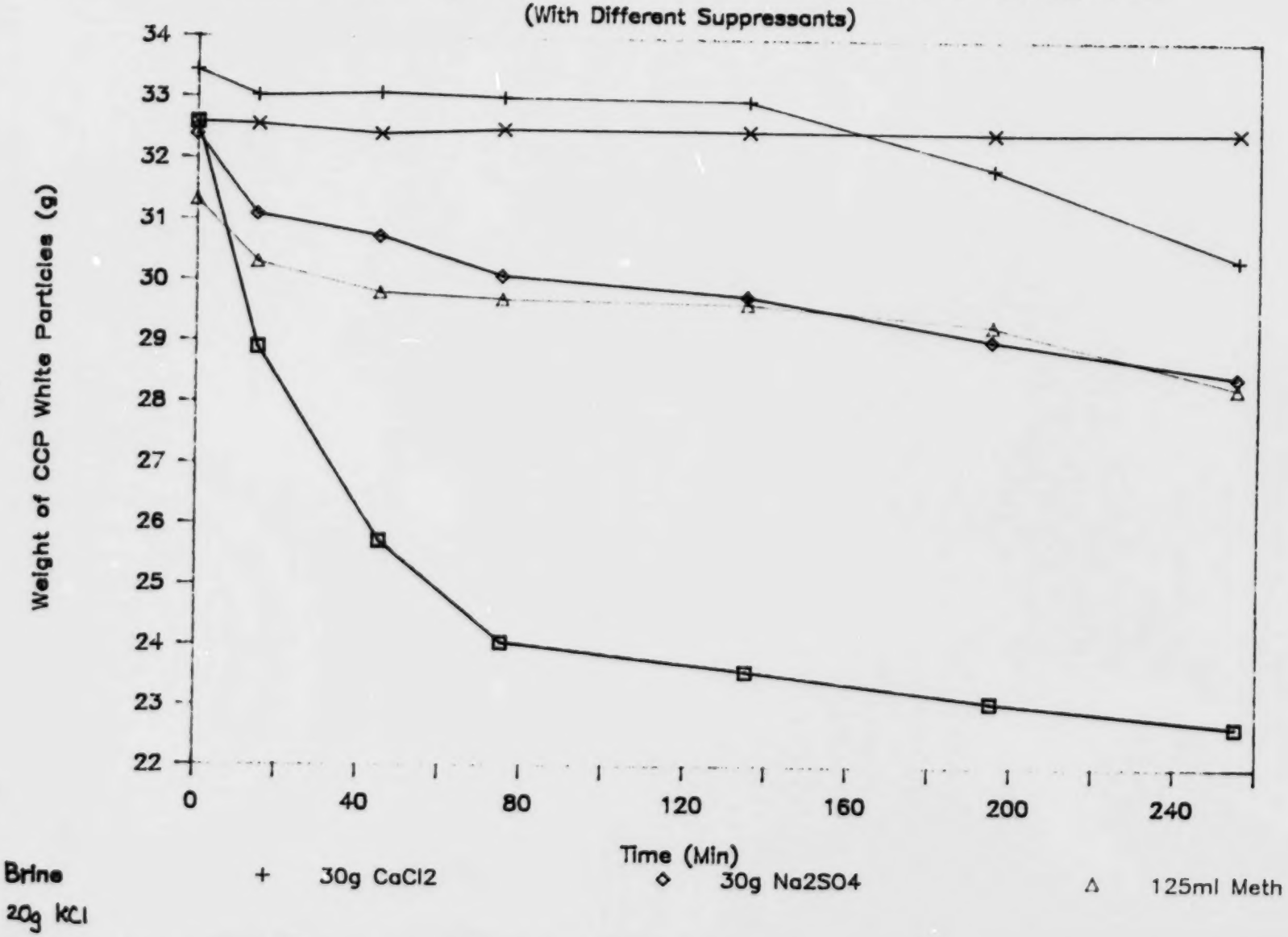


TABLE 6- Kinetics of IMC Potash in Brine

With $CaCl_2$ As Suppressant

Time (Min)	Weight of Potash Particles(g)				
	Brine	Brine + 5g $CaCl_2$	Brine + 10g $CaCl_2$	Brine + 15g $CaCl_2$	Brine + 20g $CaCl_2$
0.0	32.15	31.73	31.92	32.75	32.57
15.0	26.97	28.84	29.07	31.33	32.57
45.0	23.75	27.03	28.08	29.02	30.01
75.0	22.56	25.05	25.77	27.43	28.11
135.0	22.10	23.99	25.10	25.92	27.00
195.0	21.64	23.13	23.24	25.16	25.99
255.0	20.35	22.86	22.96	24.97	24.90

With Methanol As Suppressant

Time (Min)	Weight of Potash Particles (g)			
	Brine	Brine + 25ml Meth	Brine + 50ml Meth	Brine + 75ml Meth
0.0	32.15	32.15	32.59	32.49
15.0	26.97	30.12	31.31	31.09
45.0	23.75	27.71	28.76	29.43
75.0	22.56	26.92	27.44	28.24
135.0	22.10	25.06	26.47	28.20
195.0	21.94	23.69	25.32	27.44
255.0	20.35	23.13	24.39	26.33

With Na_2SO_4 As Suppressant

Time (Min)	Weight of Potash Particles (g)			
	Brine	Brine + 5g Na_2SO_4	Brine + 10g Na_2SO_4	Brine + 20g Na_2SO_4
0.0	32.15	32.50	32.35	32.98
15.0	26.97	28.29	28.52	28.54
45.0	23.75	26.36	26.84	26.18
75.0	22.56	24.26	25.86	24.84
135.0	22.10	23.48	24.85	24.86
195.0	21.94	22.51	23.79	24.04
255.0	20.35	21.91	23.41	23.56

With KCl As Suppressant

Time (Min)	Weight of Potash Particles			
	Brine	Brine + 5g KCl	Brine + 10g KCl	Brine + 20g KCl
0.0	32.15	31.92	32.29	32.25
15.0	26.97	29.24	30.45	31.90
45.0	23.75	26.13	28.80	31.99
75.0	22.56	25.17	28.03	31.97
135.0	22.10	23.88	27.57	31.98
195.0	21.94	23.24	26.67	31.89
255.0	20.35	23.01	26.21	31.95

Figure 14 -

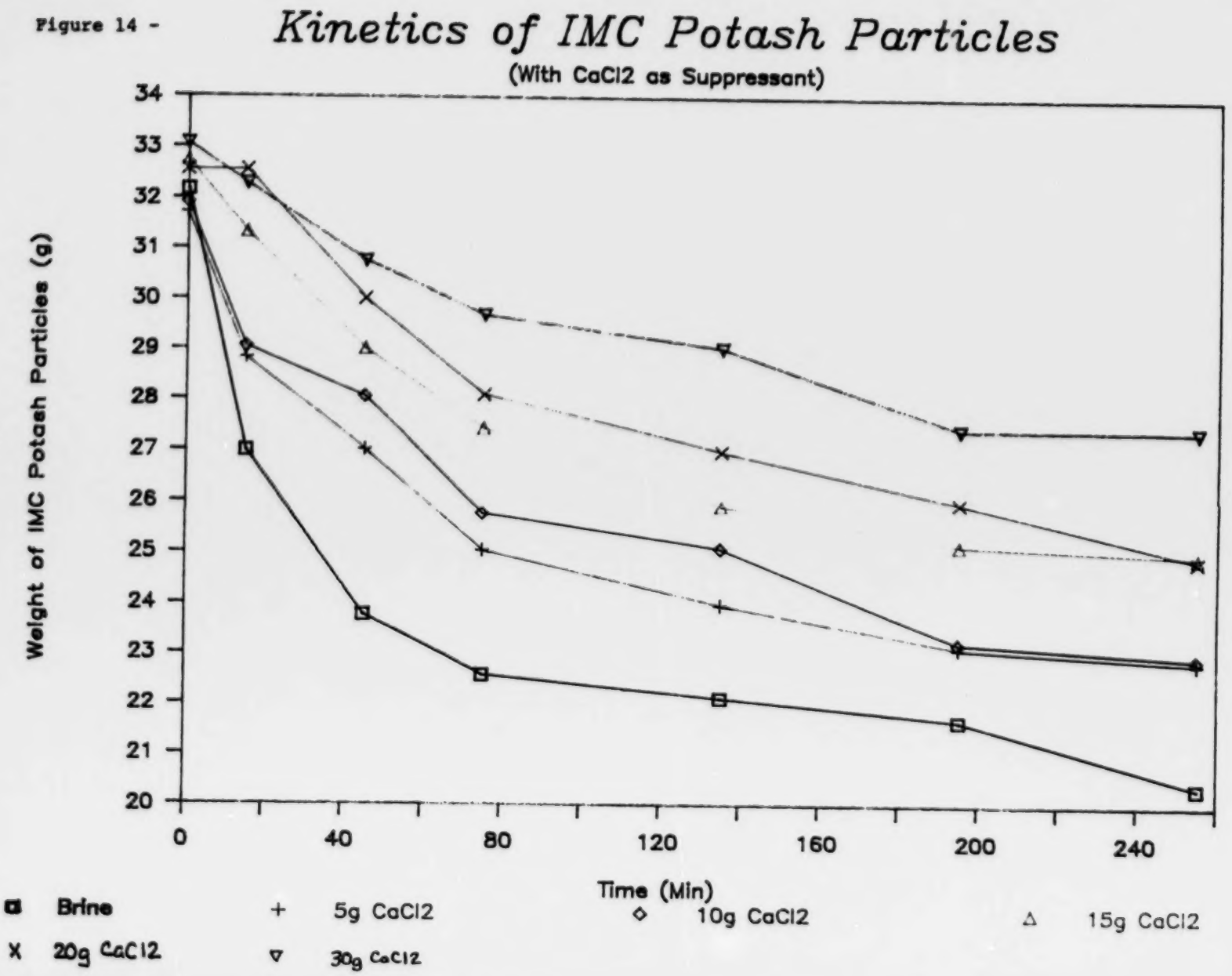

Kinetics of IMC Potash Particles
(With CaCl2 as Suppressant)
Weight of IMC Potash Particles (g)
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
0
40
80
120
160
200
240
Time (Min)
Brine
5g CaCl2
10g CaCl2
15g CaCl2
20g CaCl2
30g CaCl2

Figure 15 -

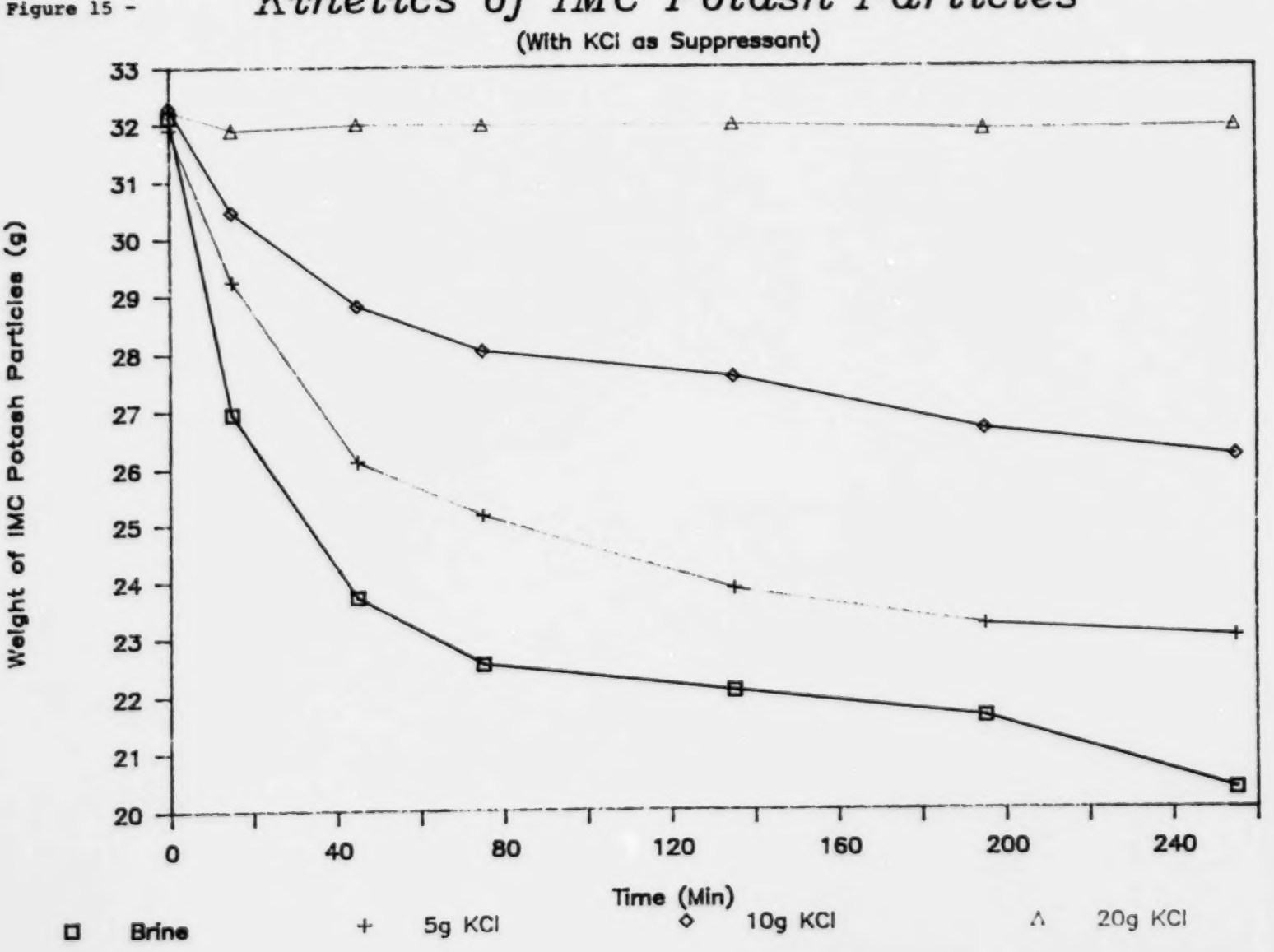

Kinetics of IMC Potash Particles
(With KCl as Suppressant)
Weight of IMC Potash Particles (g)
33
32
31
30
29
28
27
26
25
24
23
22
21
20
0
40
80
120
160
200
240
Time (Min)
Brine
5g KCl
10g KCl
20g KCl

Figure 16 -

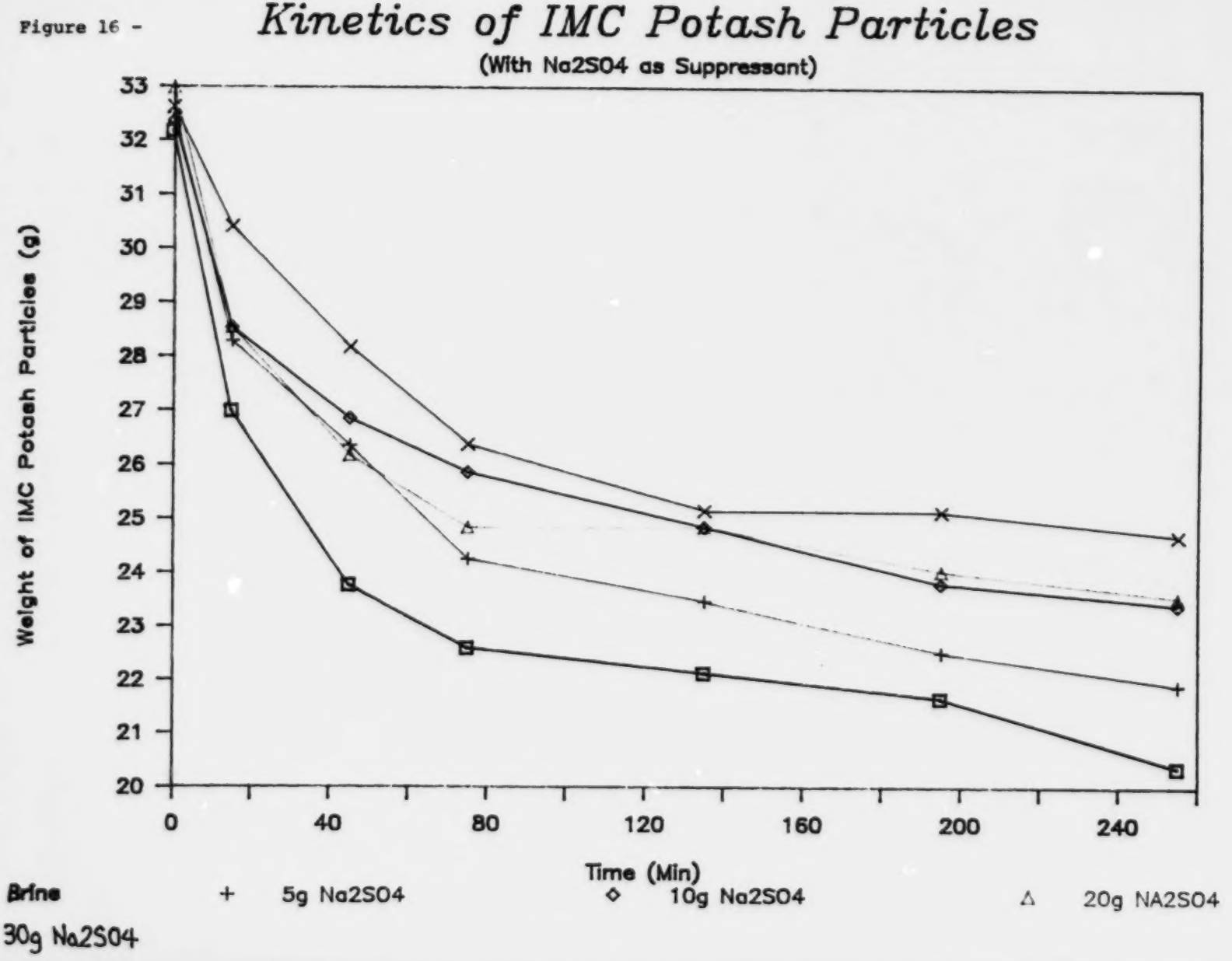

Kinetics of IMC Potash Particles
(With Na2SO4 as Suppressant)
Weight of IMC Potash Particles (g)
33
32
31
30
29
28
27
26
25
24
23
22
21
20
0
40
80
120
160
200
240
Time (Min)
Brine
5g Na2SO4
10g Na2SO4
20g NA2SO4
30g Na2SO4

Figure 17 -

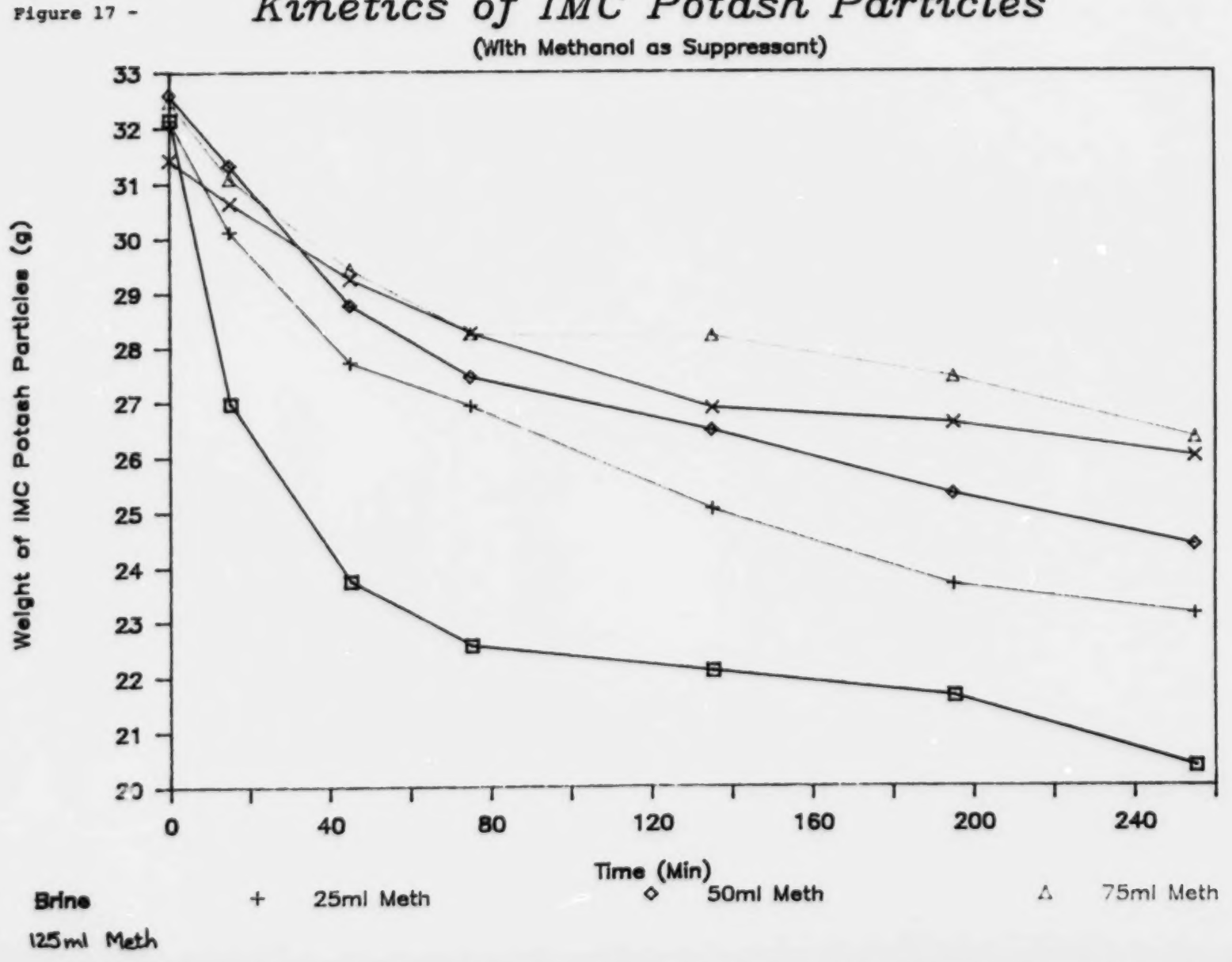

Kinetics of IMC Potash Particles
(With Methanol as Suppressant)
Weight of IMC Potash Particles (g)
33
32
31
30
29
28
27
26
25
24
23
22
21
20
0
40
80
120
160
200
240
Time (Min)
Brine
25ml Meth
50ml Meth
75ml Meth
125ml Meth

Figure 18 - *Kinetics of IMC Potash Particles*

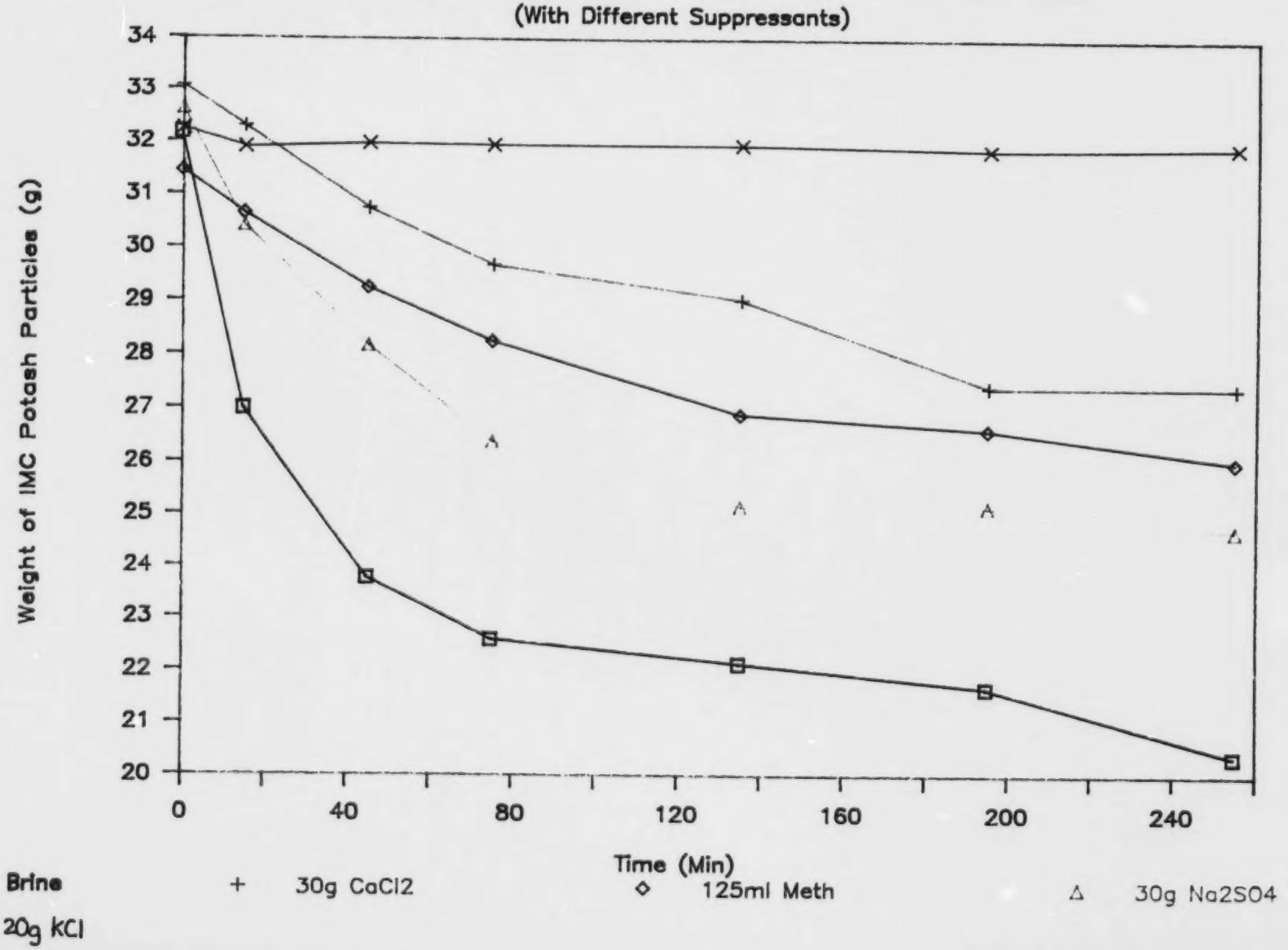


Figure 19 - *Reproducibility of CCP Red Particles*

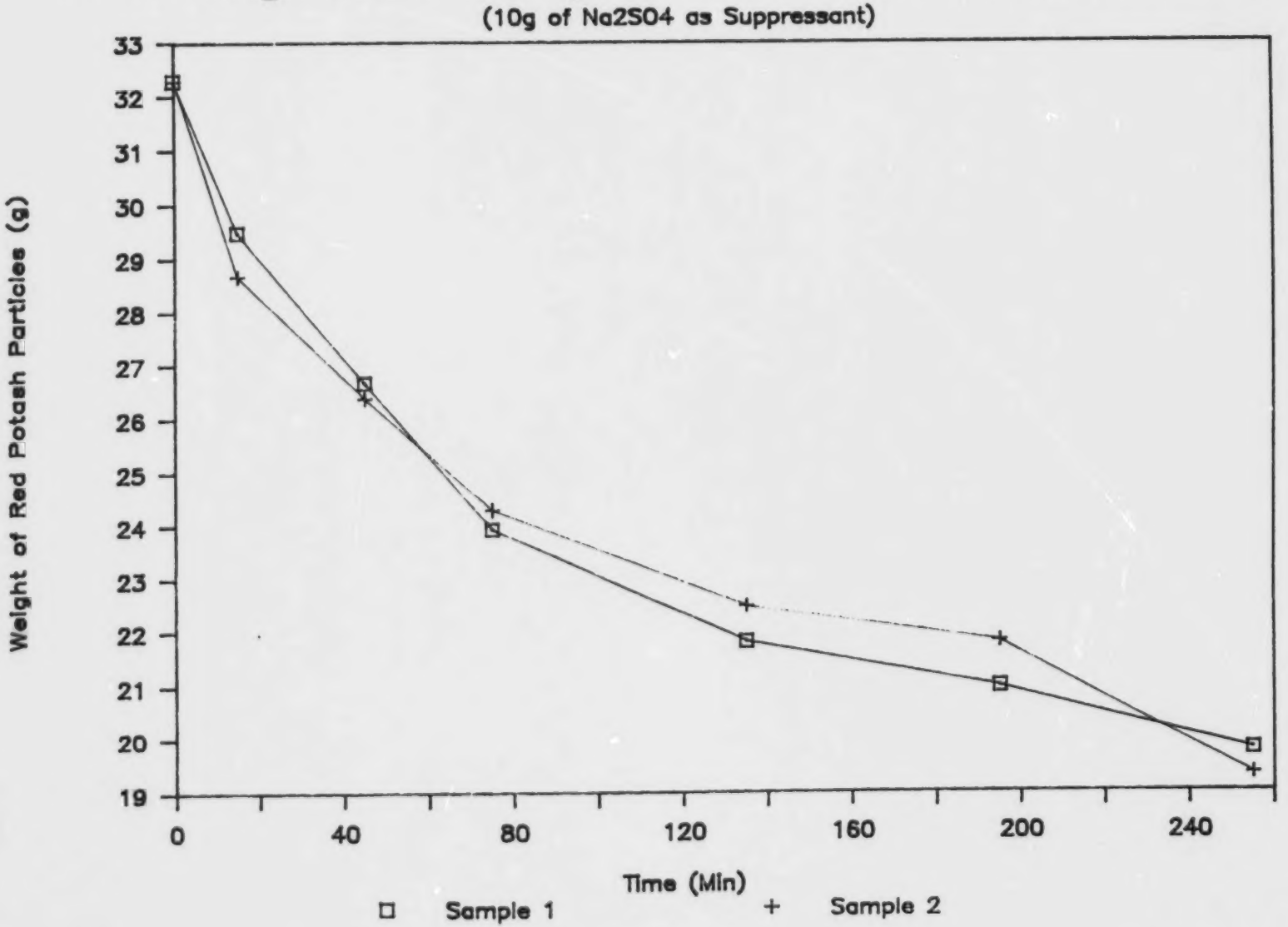


Figure 20 - *Reproducibility of CCP Red Particles*

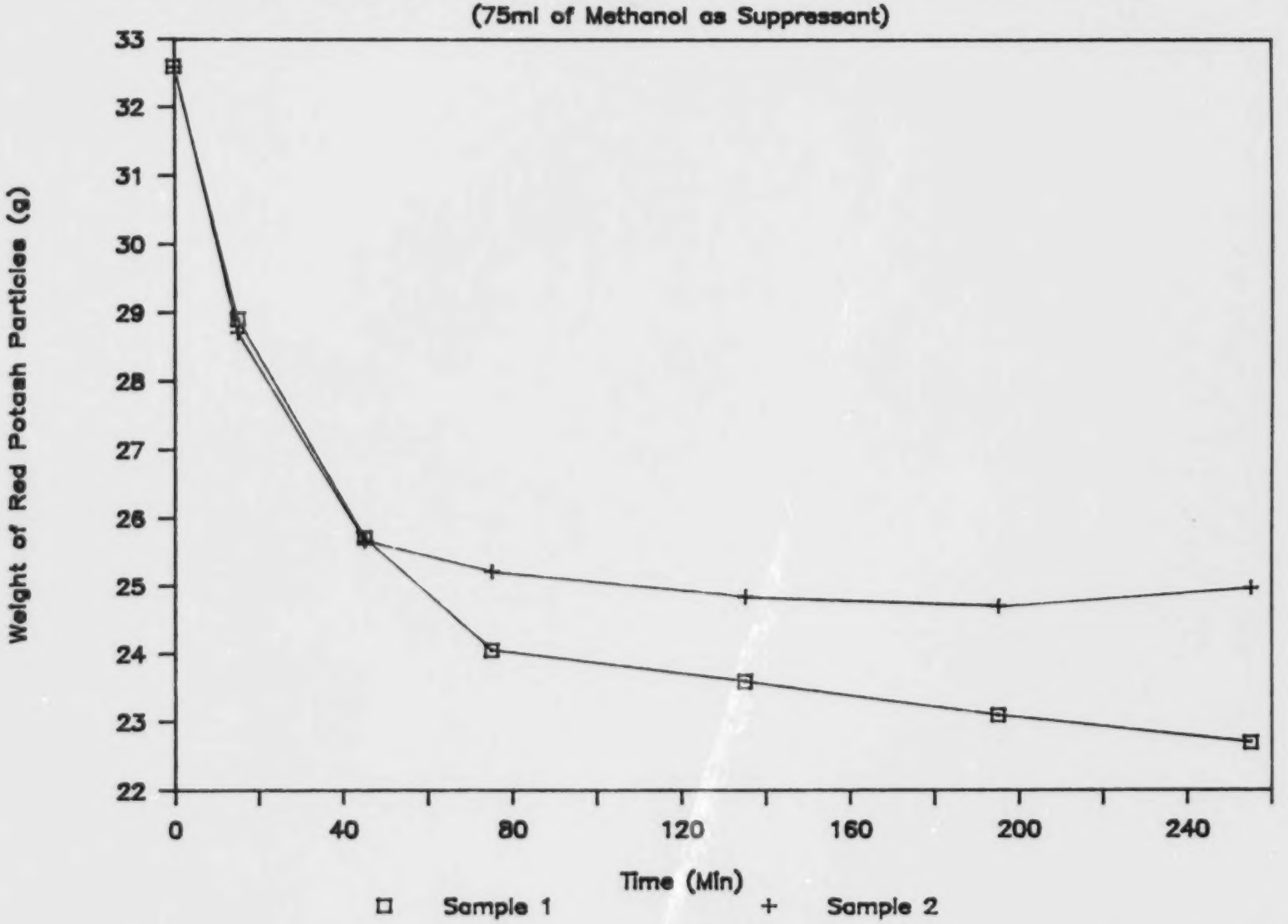


Figure 21 - *Reproducibility of CCP Red Particles*

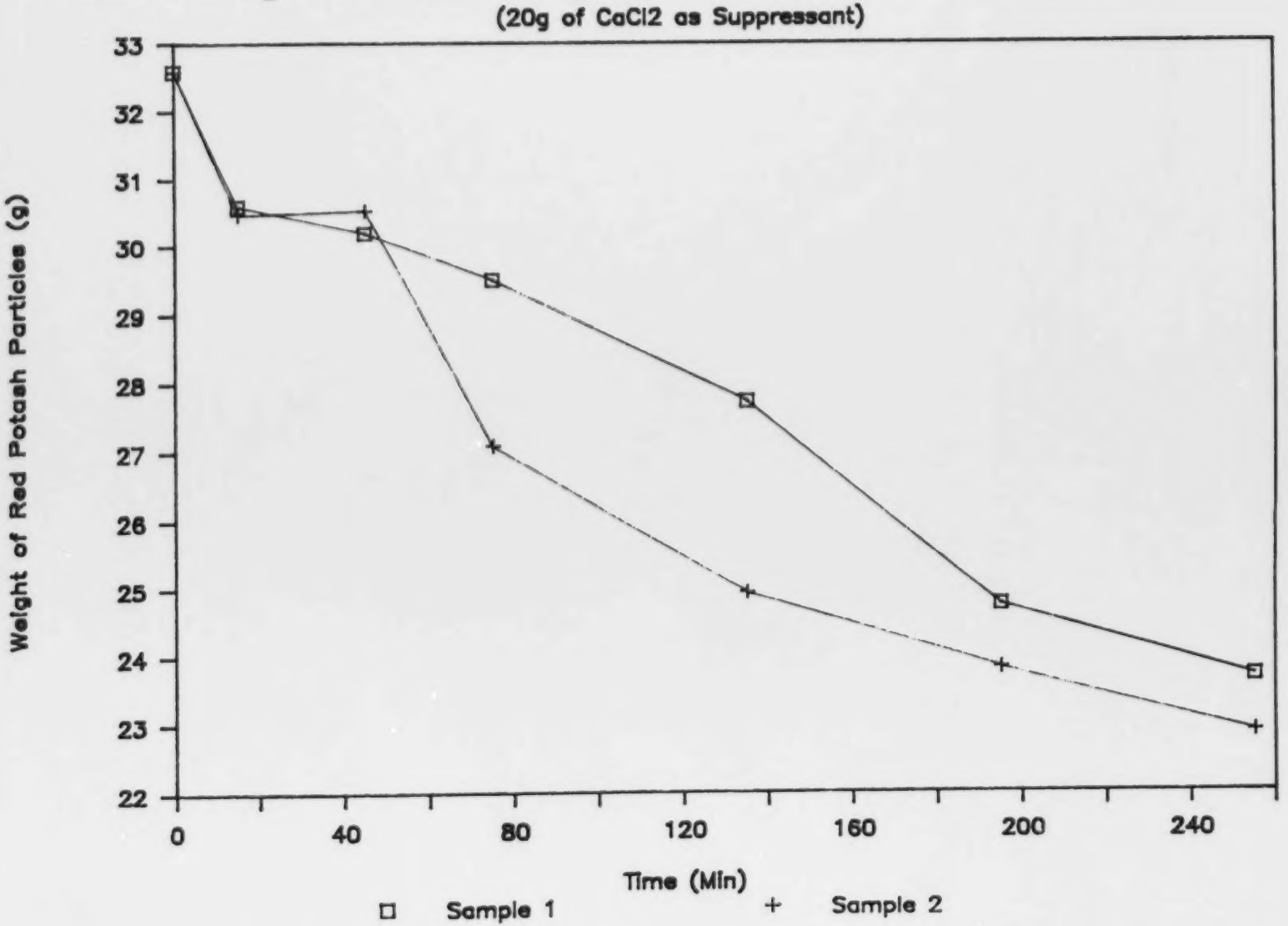


Figure 22 *Reproducibility of CCP White Particles*

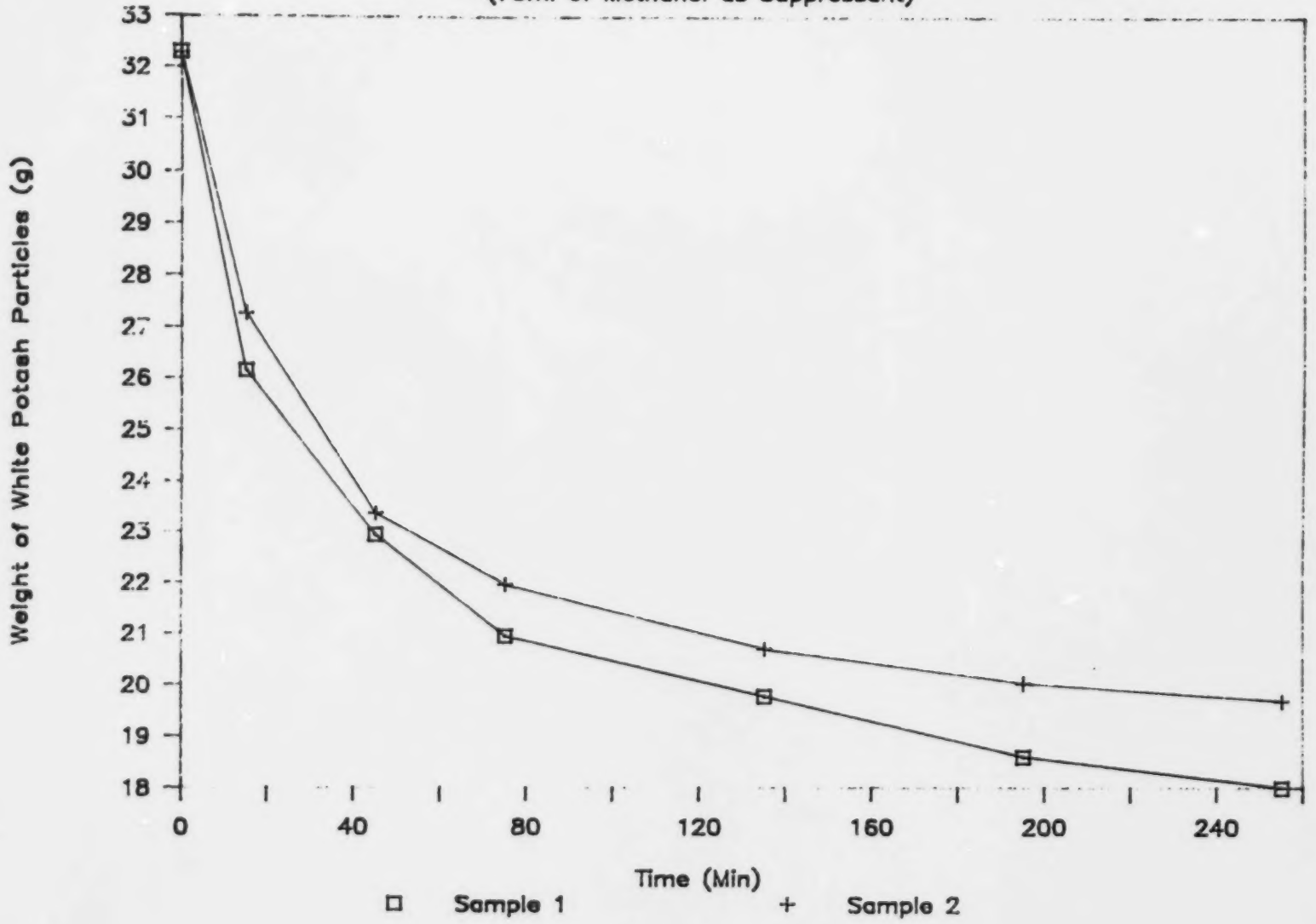


Figure 23 - *Reproducibility of CCP White Particles*

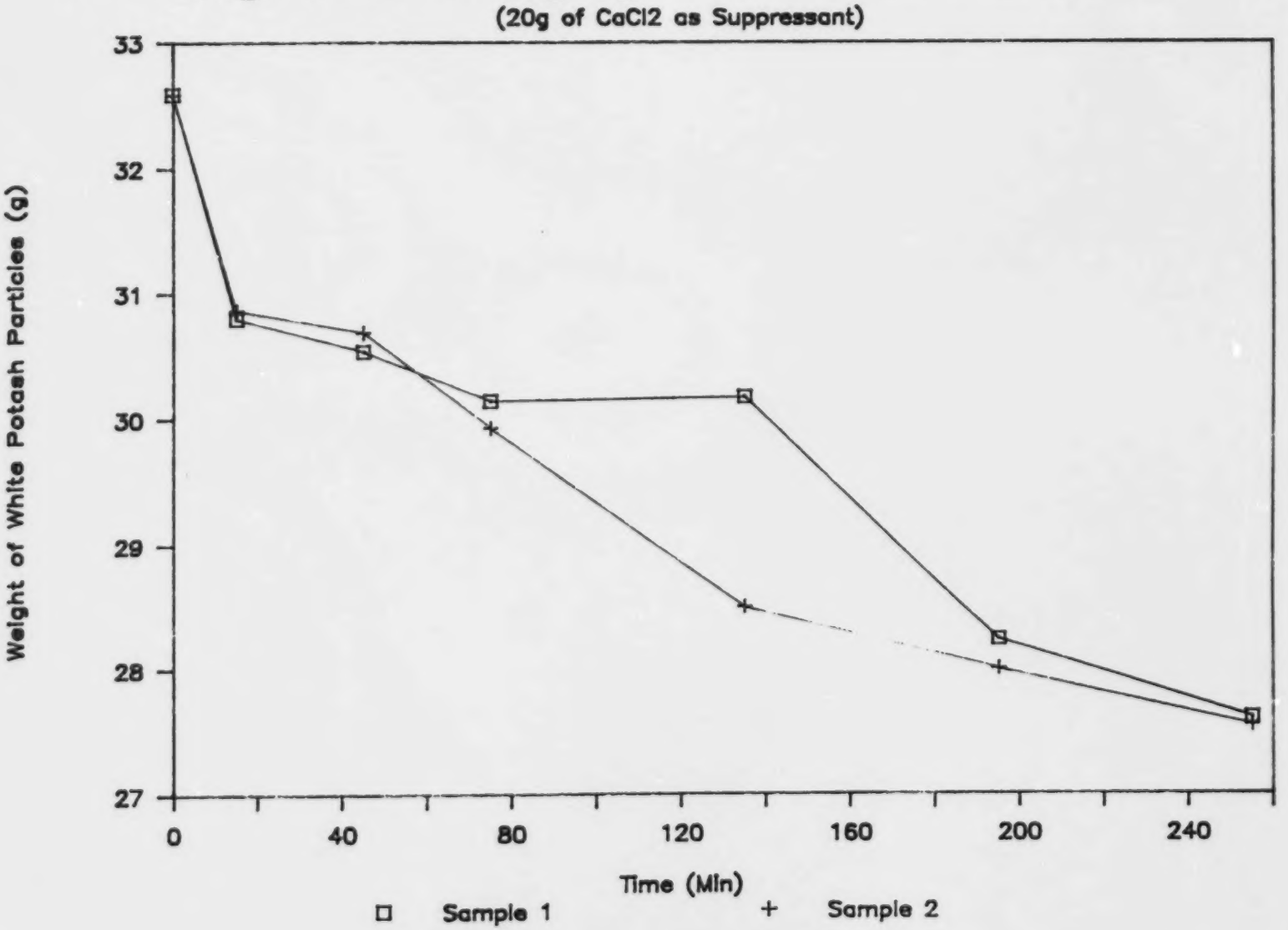


Figure 24 - *Reproducibility of CCP White Particles*

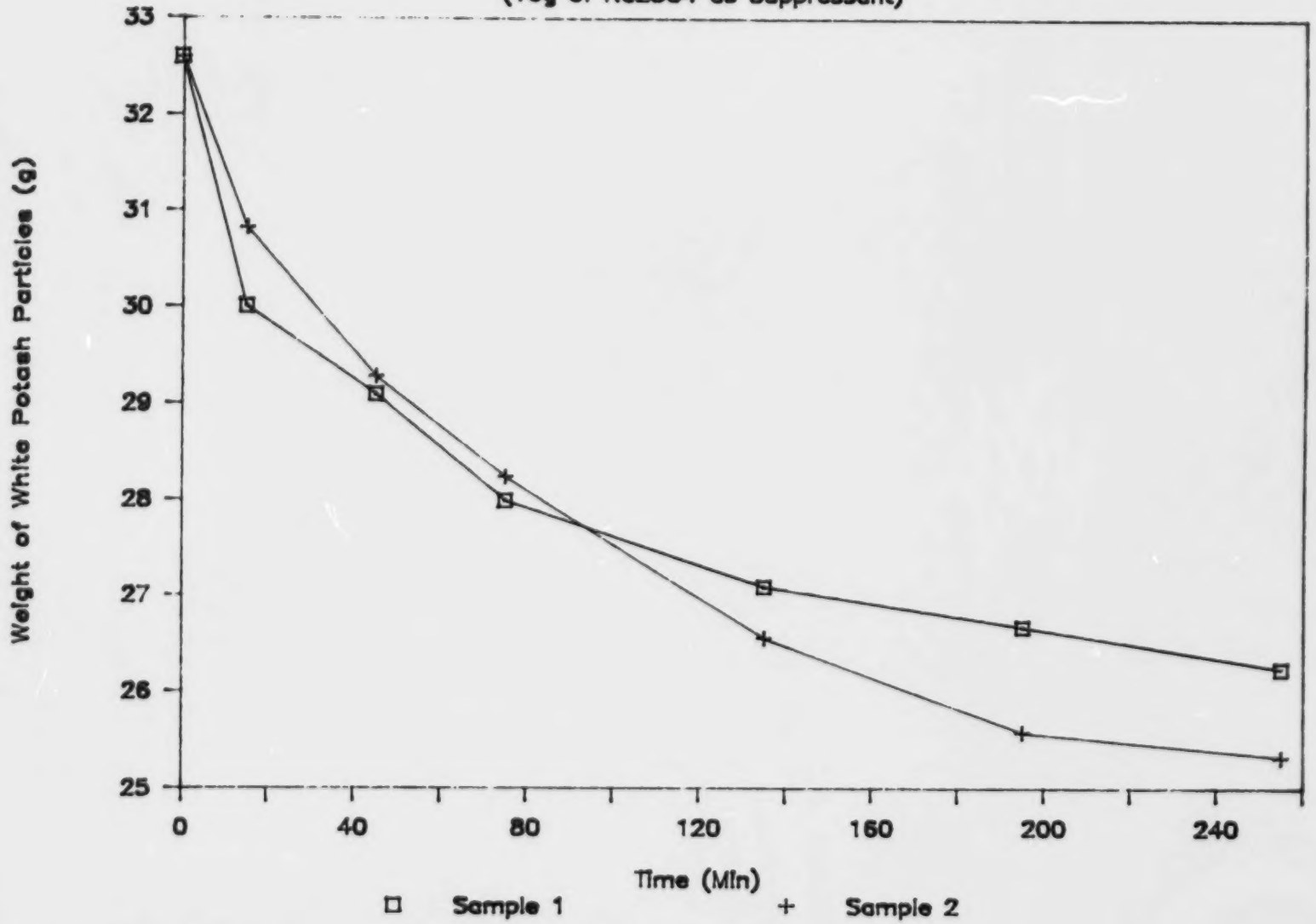


Figure 25 - *Reproducibility of IMC Potash Particles*

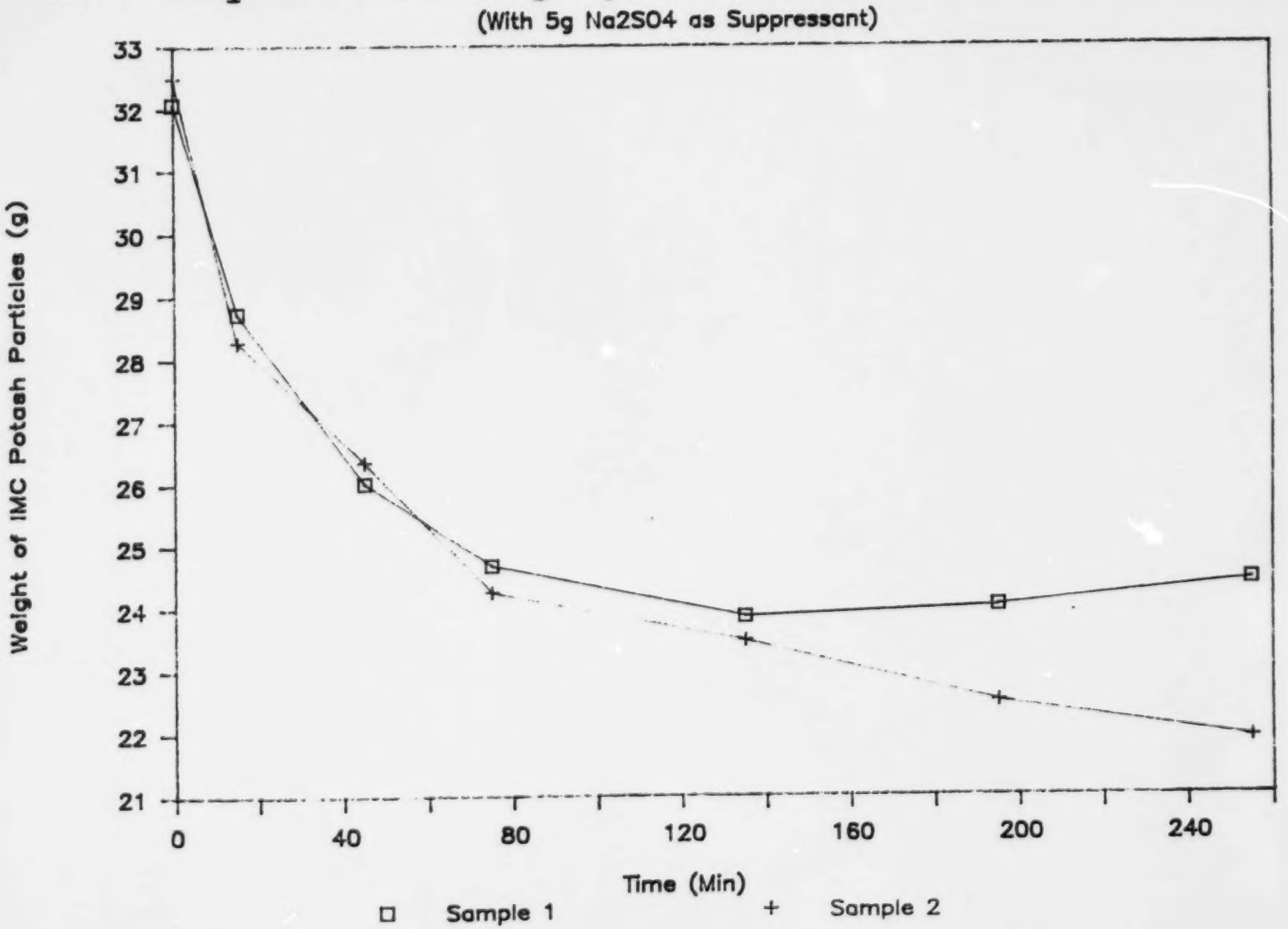


Figure 26 - *Reproducibility of IMC Potash Particles*

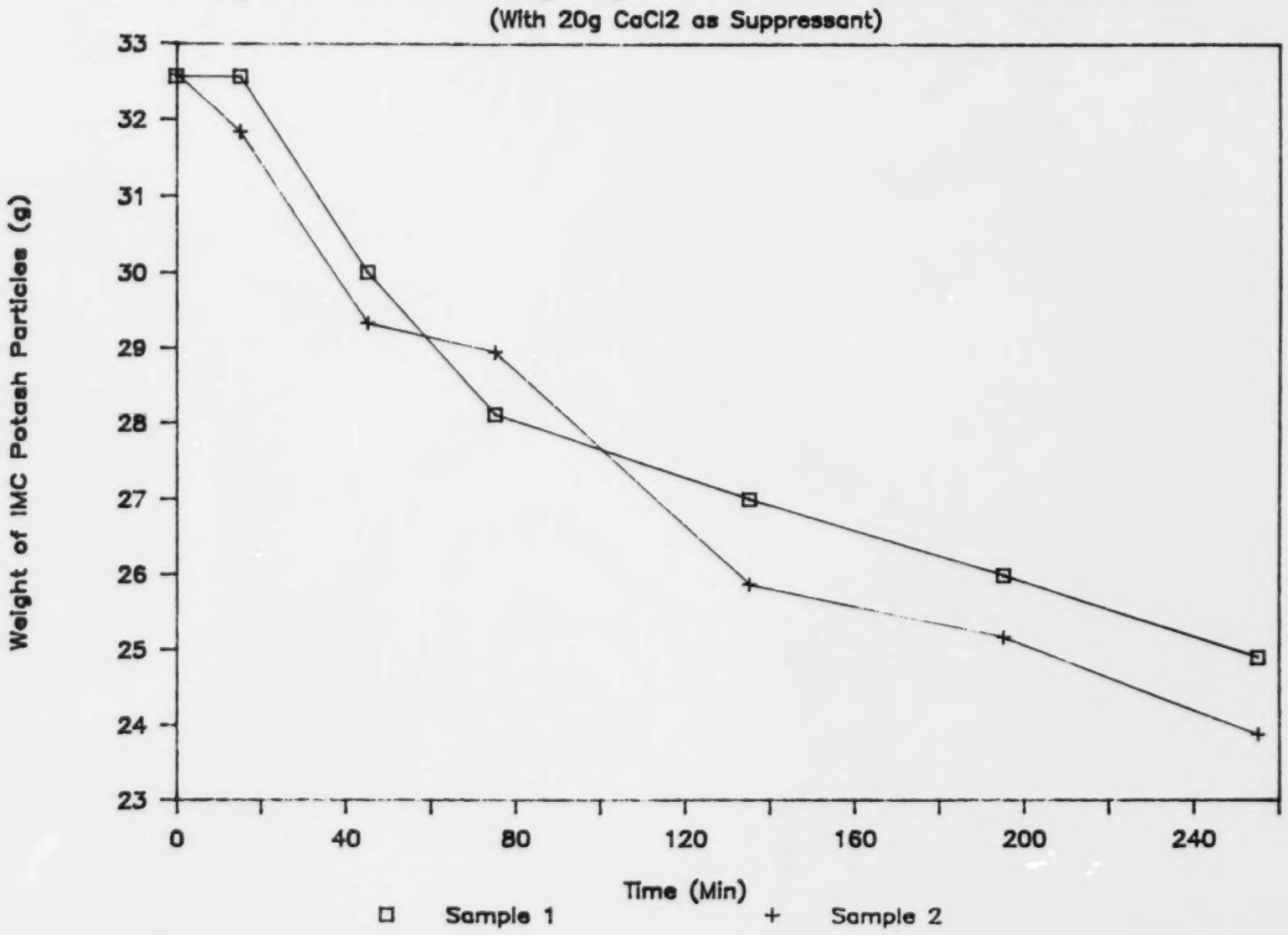


Figure 27 - *Reproducibility of IMC Potash Particles*

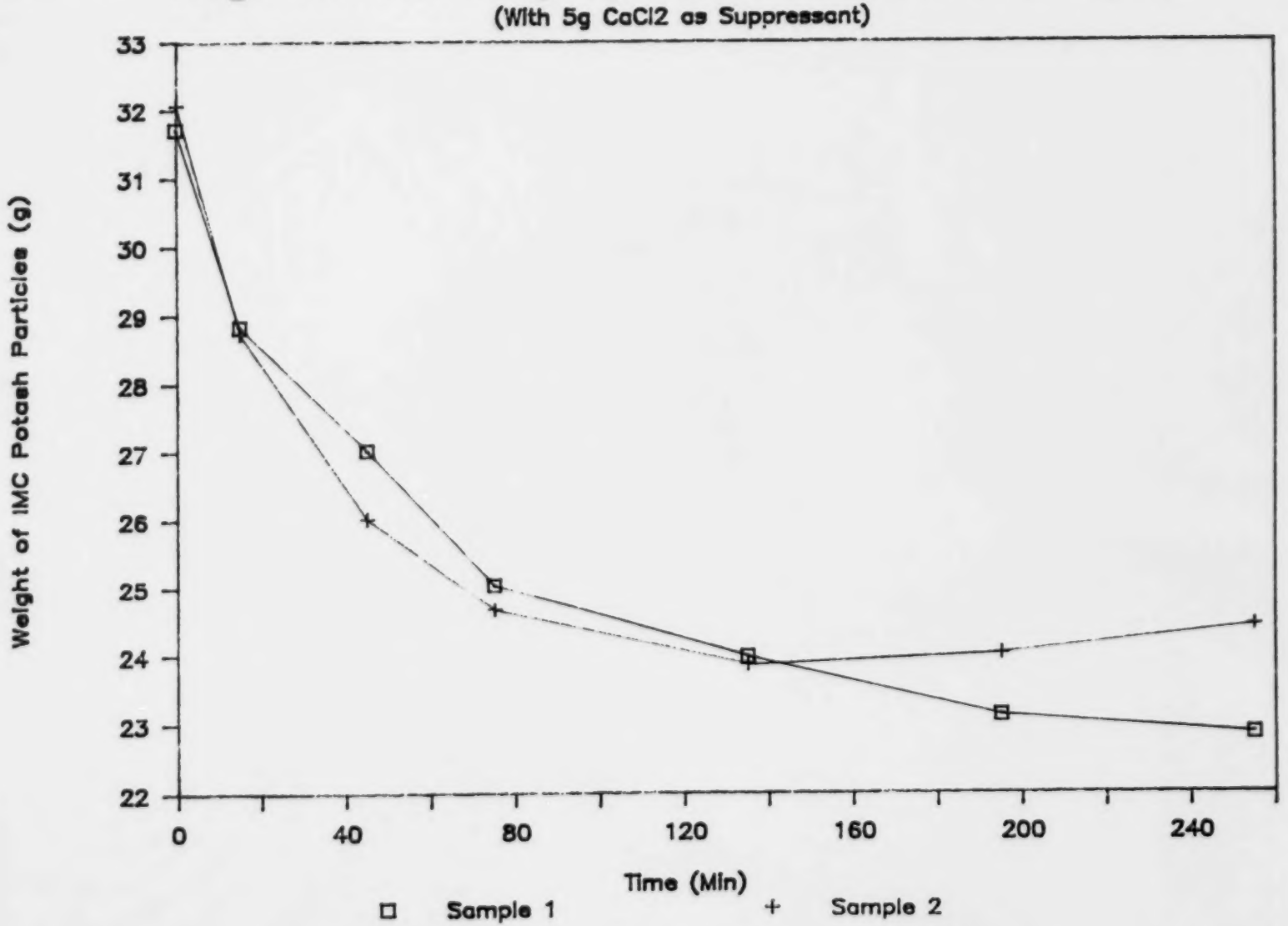


Figure 28 - *Reproducibility of IMC Potash Particles*

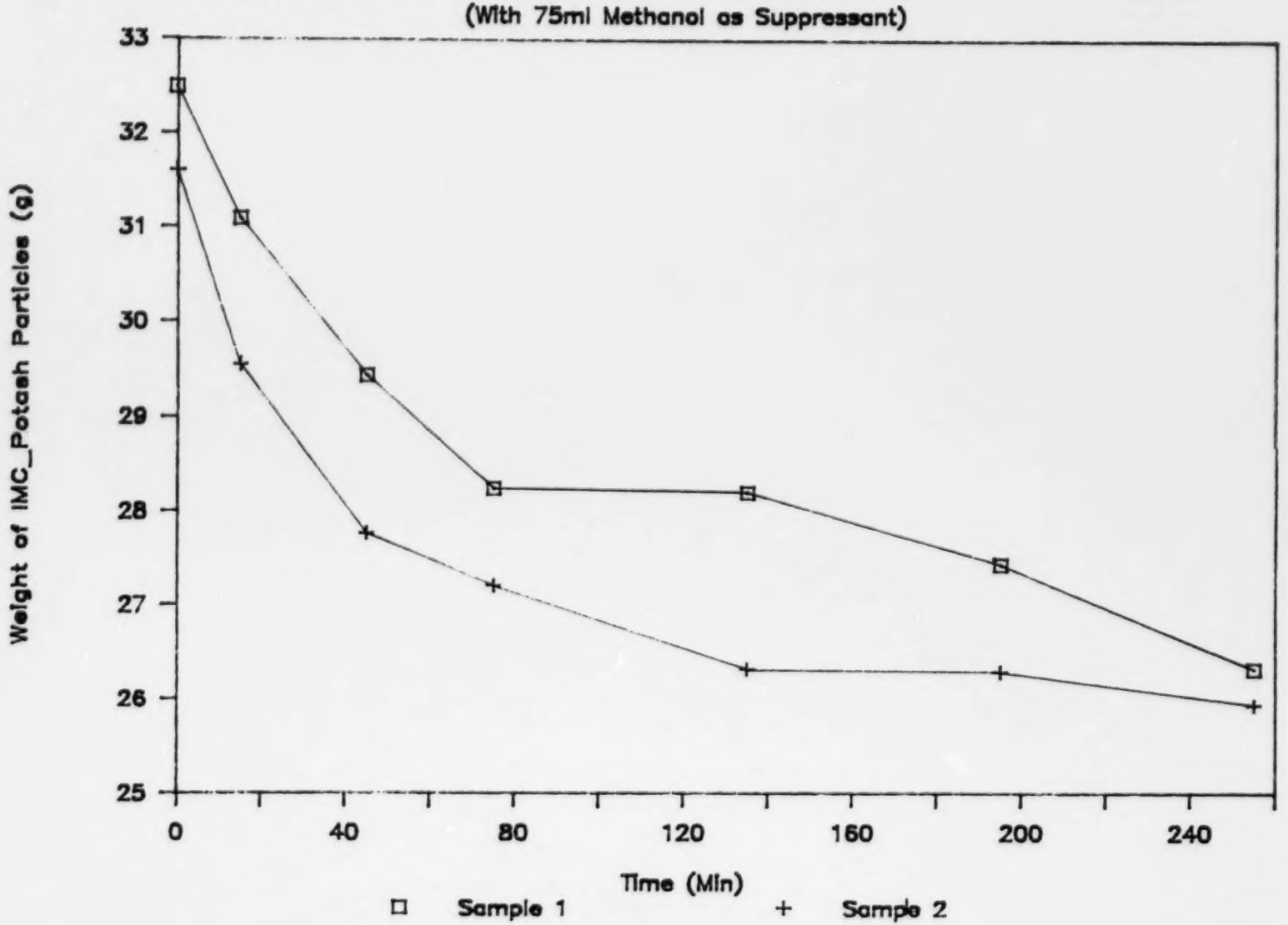


TABLE 7 - Reproducibility of CCP Results
(Red Samples)

75ml of Methanol as Suppressant

Time (Min)	Wt. of Potash (g)	
	Sample 1	Sample 2
0.0	32.60	32.60
15.0	28.91	28.72
45.0	25.72	25.68
75.0	24.05	25.22
135.0	23.60	24.85
195.0	23.10	24.71
255.0	22.70	25.00

20g of CaCl2 as Suppressant

Time (Min)	Wt. of Potash (g)	
	Sample 1	Sample 2
0.0	32.60	32.60
15.0	30.60	30.48
45.0	30.20	30.54
75.0	29.50	27.10
135.0	27.75	24.95
195.0	24.76	23.83
255.0	23.70	22.88

10g of Na2SO4 as Suppressant

Time (Min)	Wt. of Potash (g)	
	Sample 1	Sample 2
0.0	32.30	32.30
15.0	29.49	28.68
45.0	26.67	26.38
75.0	23.93	24.29
135.0	21.82	22.49
195.0	21.00	21.82
255.0	19.80	19.33

TABLE 8- Reproducibility of CCP Results
(White Samples)

75ml of Methanol as Suppressant

Time (Min)	Wt. of Potash (g)	
	Sample 1	Sample 2
0.0	32.30	32.30
15.0	26.15	27.27
45.0	22.93	23.37
75.0	20.93	21.95
135.0	19.78	20.70
195.0	18.60	20.04
255.0	18.00	19.70

20g of CaCl2 as Suppressant

Time (Min)	Wt. of Potash (g)	
	Sample 1	Sample 2
0.0	32.60	32.60
15.0	30.80	30.87
45.0	30.54	30.69
75.0	30.14	29.93
135.0	30.18	28.51
195.0	28.24	28.00
255.0	27.61	27.55

10g of Na2SO4 as Suppressant

Time (Min)	Wt. of Potash (g)	
	Sample 1	Sample 2
0.0	32.60	32.60
15.0	30.01	30.82
45.0	29.10	29.28
75.0	28.00	28.24
135.0	27.10	26.55
195.0	26.67	25.58
255.0	26.24	25.33

TABLE 9 - Reproducibility of IMC Results

20g of $CaCl_2$ as Suppressant

Time (Min)	Wt. of IMC Potash (g)	
	Sample 1	Sample 2
0.0	32.57	32.60
15.0	32.57	31.84
45.0	30.01	29.34
75.0	28.11	28.95
135.0	27.00	25.87
195.0	25.99	25.17
255.0	24.90	23.88

75ml of Methanol as Suppressant

Time (Min)	Wt. of IMC Potash (g)	
	Sample 1	Sample 2
0.0	32.49	32.69
15.0	31.09	29.55
45.0	29.43	27.77
75.0	28.24	27.21
135.0	28.20	26.32
195.0	27.44	26.30
255.0	26.33	25.95

20g of Na_2SO_4 as Suppressant

Time (Min)	Wt. of IMC Potash (g)	
	Sample 1	Sample 2
0.0	32.46	32.98
15.0	27.99	28.54
45.0	26.70	26.18
75.0	24.66	24.84
135.0	23.66	24.86
195.0	22.62	24.04
255.0	22.44	23.56

very close considering the experimental error and the fact that initial samples for each experiment do not have exactly the same composition. Only Figure 26 shows significant variation between the two sets of data points and that could be as a result of the difference in initial composition of the samples taken.

5.1b Static Test at Different Temperatures

Static test was carried out at 4 different temperatures of 15, 25, 35 and 45°C. Only IMC particles were used for this set of experiments. Table 10 and Figure 29 show the rate of dissolution of IMC potash particles in brine at four different temperatures. There is no significant difference between these 4 set of data. At all 4 temperatures, the majority of dissolution takes place in the first 75 minutes and the system reaches its equilibrium conditions thereafter.

Low amounts of suppressants were then added to the brine. For each specific amount of suppressant, the curves were compared at four different temperatures. Tables 11 and 12 contain the relevant data. Dissolution of these particles in brine* 5 g KCl and brine + 5 g of $CaCl_2$ have similar trends. Rates of dissolution were higher at higher temperatures (Figures 30 and 31). In cases of brine + 5 g Na_2SO_4 and brine + 25 mL of Methanol, up to the time of 75 minutes, similar trends were observed (Figures 32 and 33). From this time on, the temperature of 45°C gives a better result than the temperature of 35°C. The equilibrium was achieved at 45°C sooner than the equilibrium at 35°C.

At each temperature, the dissolution rate of IMC particles in brine + suppressants were compared. Table 13 indicates the data at 15 and 25°C. Tables 14 and 15 tabulate the results at 35 and 45°C for both low and high amounts of suppressants. For low amounts of suppressant, the trend is not very clear especially at higher temperatures. At 15°C the only effective suppressants are methanol and sodium sulfate (Figure 34). At the temperature 25°C, all of

Table 10 - Kinetics of IMC Potash in Brine at Different Temperatures

Time Min	Weight of Particles (g)			
	T = 15C	T = 25C	T = 35C	T = 45C
0	32.58	32.15	32.98	31.56
15	27.80	26.97	26.89	25.74
45	25.70	23.75	24.86	23.32
75	23.72	22.56	23.35	22.88
135	22.56	22.10	22.62	23.17
195	22.15	21.64	22.45	23.08
255	21.74	20.35	22.43	23.23

Figure 29 -

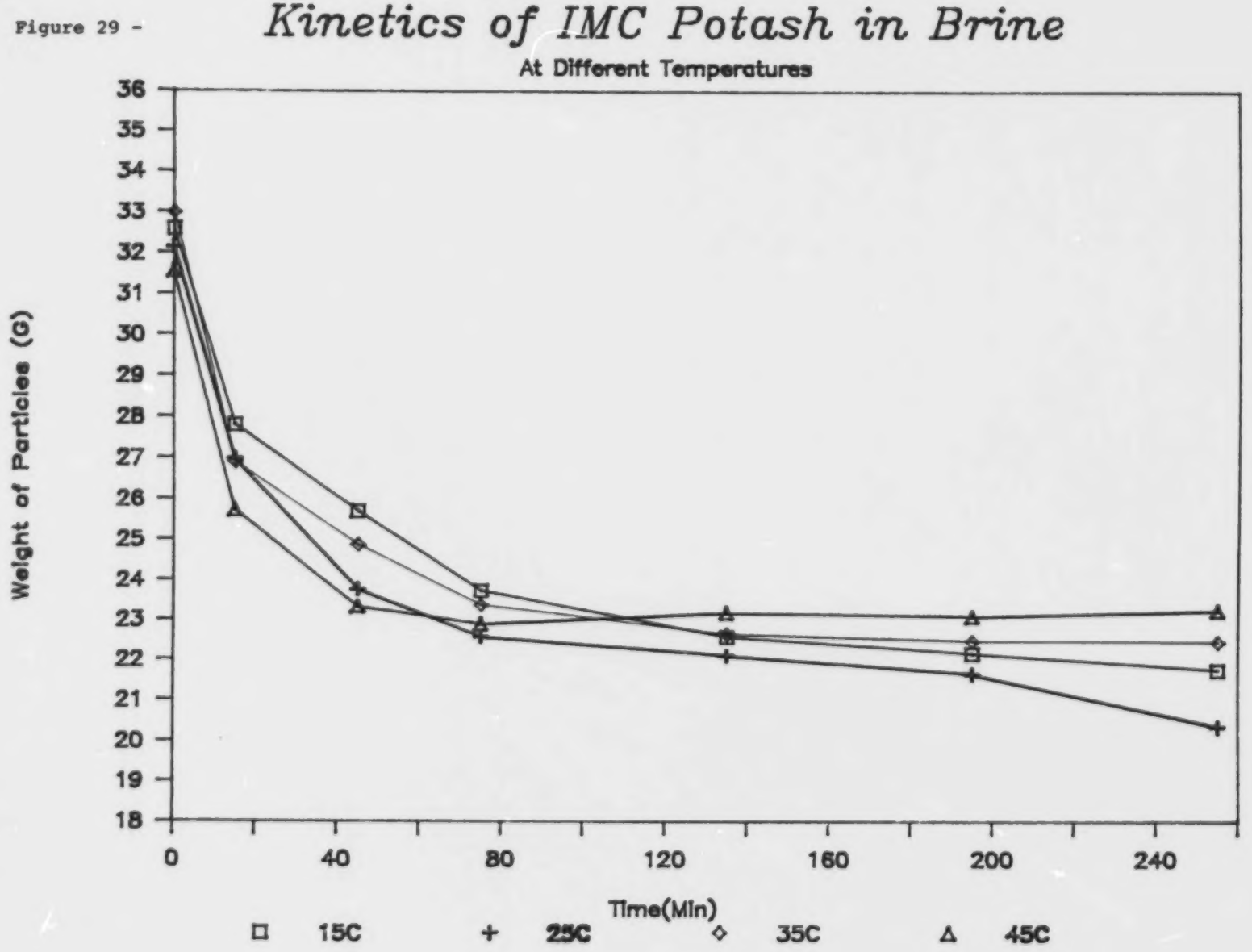

Kinetics of IMC Potash in Brine
At Different Temperatures
Weight of Particles (G)
36
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
19
18
0
40
80
120
160
200
240
Time(Min)
15C
25C
35C
45C

Table 11 - Kinetics of IMC Potash in Brine + Suppressant at Different Temperatures

11a - (suppressant = 5 g KCl)

Time Min	Weight of Particles (g)			
	T = 15C	T = 25C	T = 35C	T = 45C
0	32.49	31.92	32.24	32.23
15	30.20	29.24	28.28	26.07
45	28.10	26.13	25.10	22.44
75	25.94	25.17	24.83	21.03
135	25.00	23.88	23.64	20.24
195	24.83	23.24	23.37	19.87
255	24.34	23.01	22.89	19.70

11b - (suppressant = 25 mL Methanol)

Time Min	Weight of Particles (g)			
	T = 15C	T = 25C	T = 35C	T = 45C
0	32.50	32.15	31.58	31.62
15	31.42	30.12	27.63	28.46
45	29.15	27.71	25.48	25.78
75	26.98	26.92	23.20	23.39
135	26.33	25.06	21.52	23.23
195	24.99	23.69	20.25	22.99
255	24.80	23.13	20.16	22.09

Table 12 - Kinetics of IMC Potash in Brine + Suppressant at Different Temperatures

12a - (suppressant = 5 g $CaCl_2$)

Time Min	Weight of Particles (g)			
	T = 15C	T = 25C	T = 35C	T = 45C
0	31.43	31.73	32.30	31.58
15	29.28	28.84	27.72	24.78
45	27.20	27.03	25.03	22.24
75	25.05	25.05	23.02	20.82
135	23.73	23.99	21.39	19.95
195	22.74	23.13	20.41	19.82
255	21.52	22.86	20.12	19.65

12b - (suppressant = 5 g Na_2SO_4)

Time Min	Weight of Particles (g)			
	T = 15C	T = 25C	T = 35C	T = 45C
0	33.9	32.50	31.78	31.98
15	28.99	29.29	27.90	26.53
45	26.54	26.36	24.61	24.67
75	24.50	24.26	21.95	22.34
135	23.12	23.48	20.62	21.84
195	22.68	22.51	20.00	21.82
255	21.23	21.91	20.00	21.80

Figure 30 - *Kinetics of IMC Potash in Brine+Suppr*

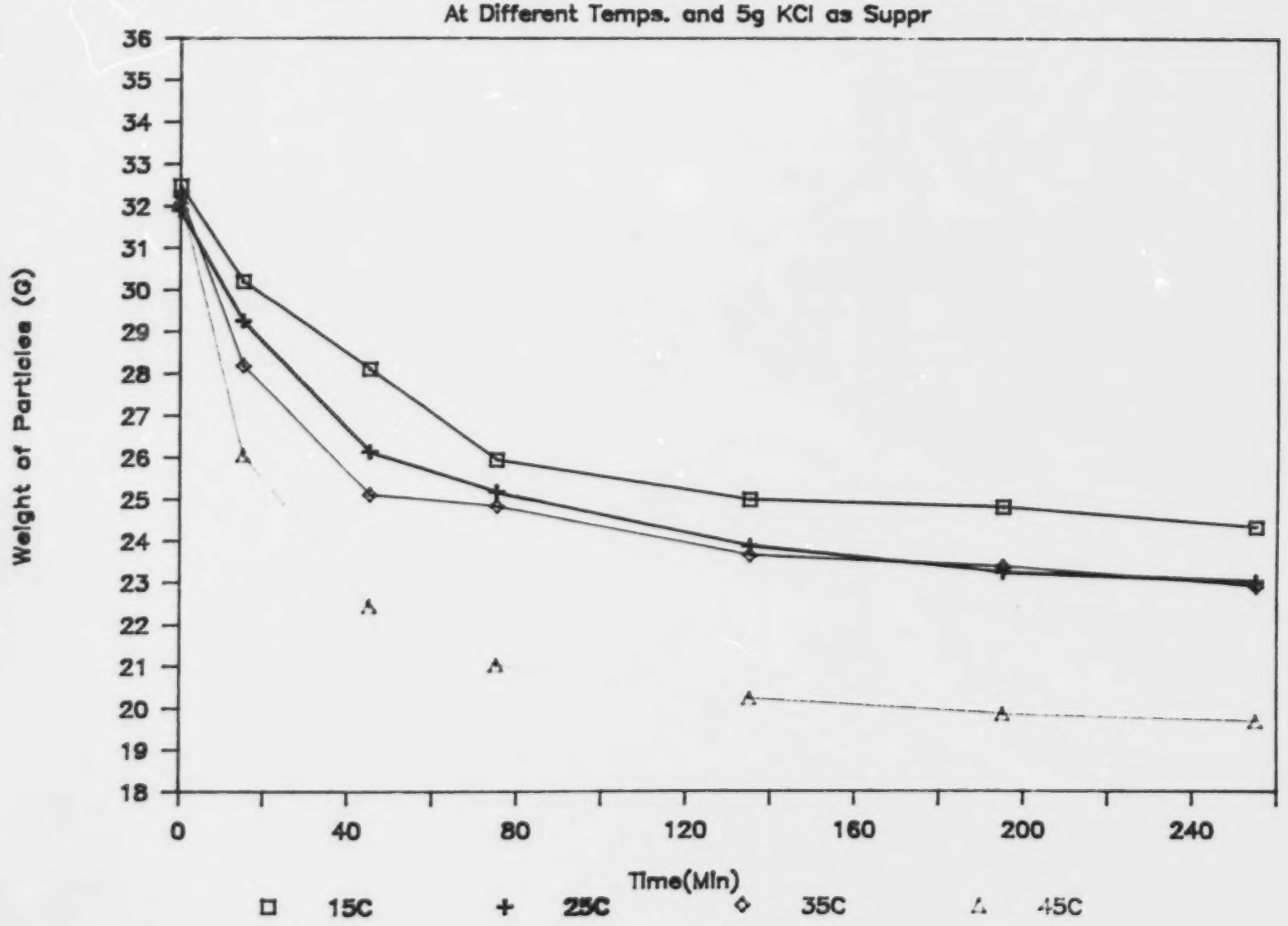


Figure 31 - *Kinetics of IMC Potash in Brine+Suppr*

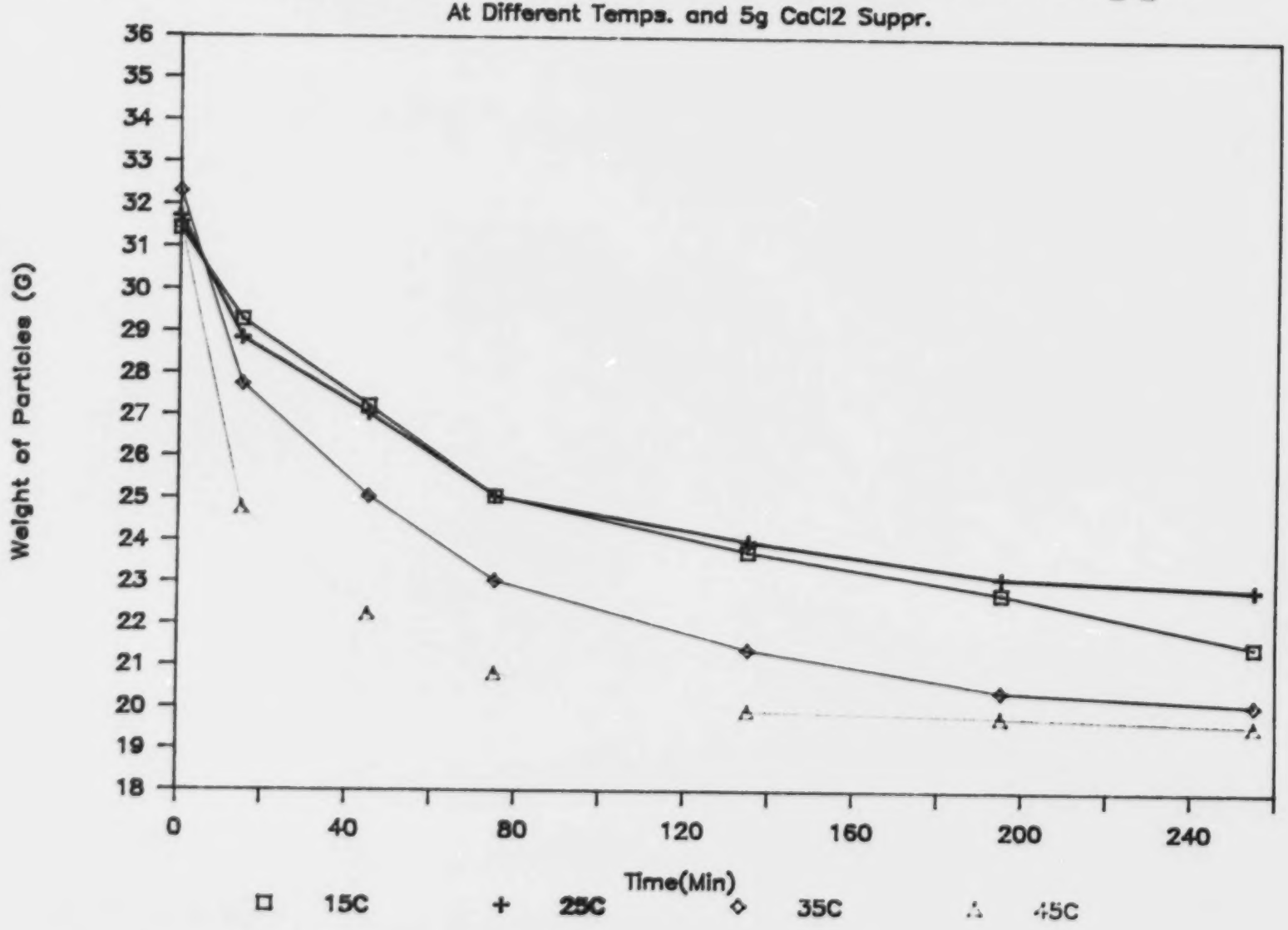


Figure 32 - *Kinetics of IMC Potash in Brine+Suppr*

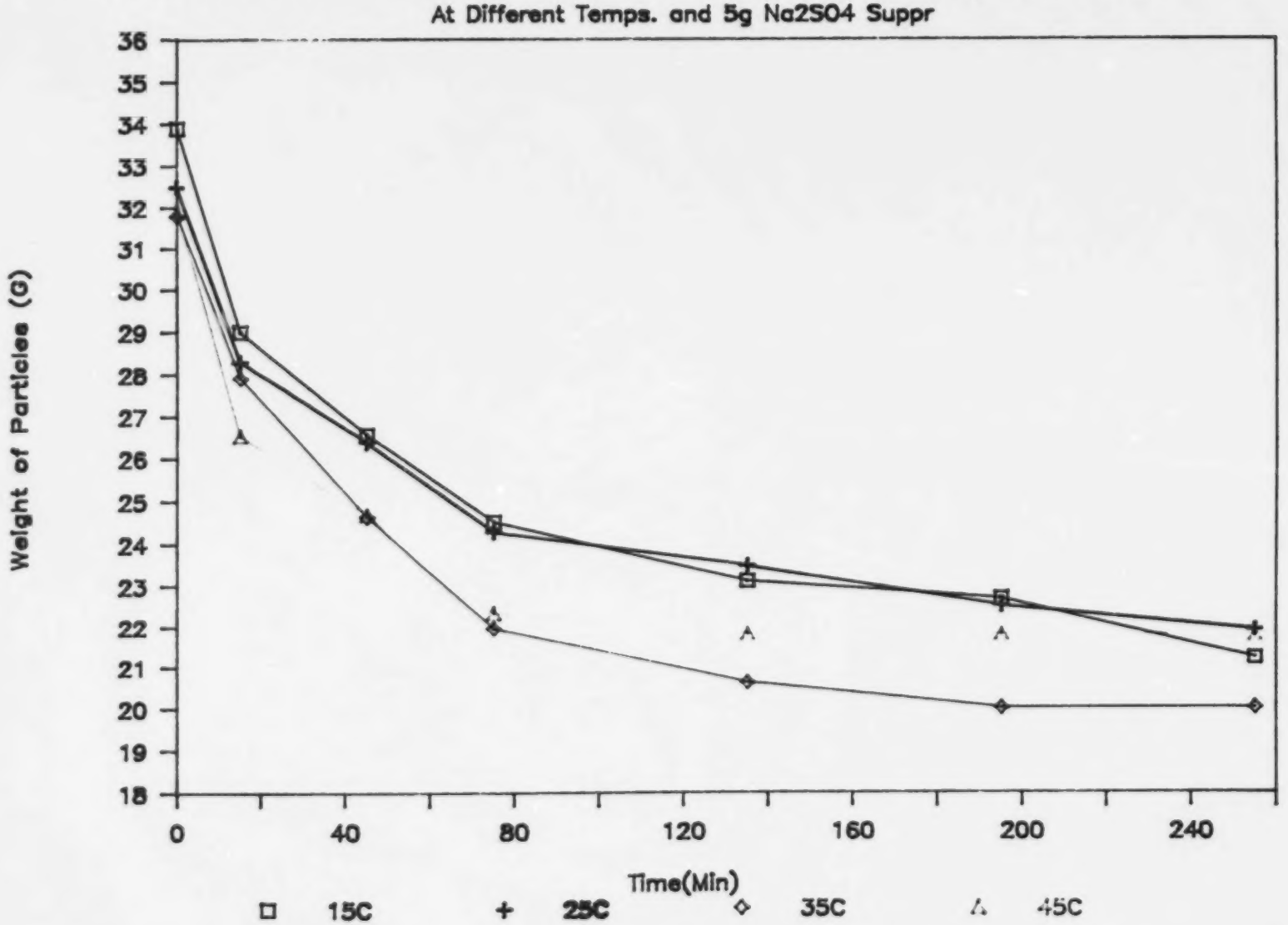


Figure 33 - *Kinetics of IMC Potash in Brine+Suppr*

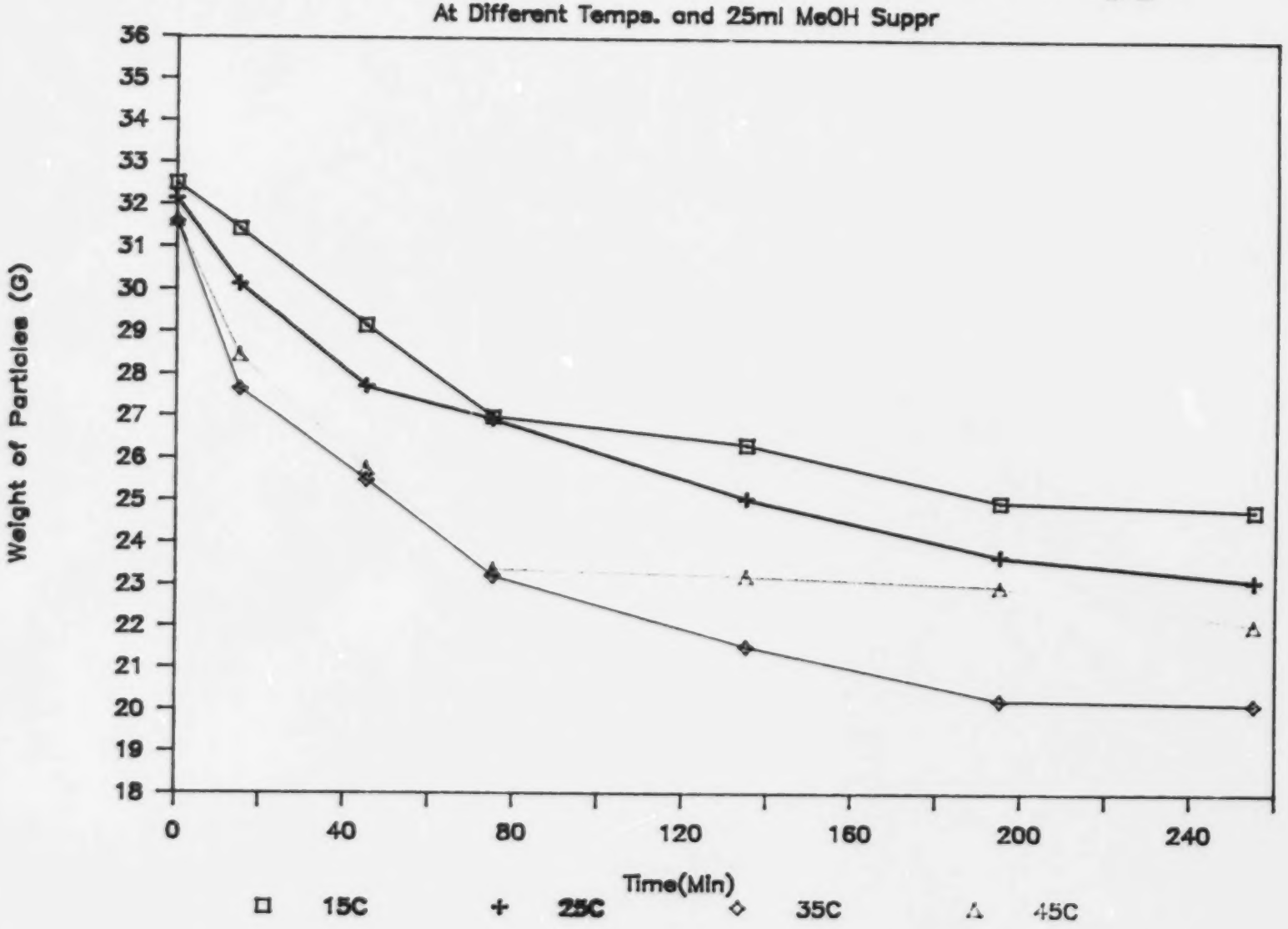


Table 13 - Kinetics of IMC Potash in Brine + Suppressants
T = 15°C

Time Min	Weight of Particles (g)				
	Brine +	Brine + 5 g $CaCl_2$	Brine + 5 g KCl	Brine + 5 g Na_2SO_4	Brine + 25 mL MEOH
0	32.58	32.24	32.06	33.9	32.50
15	27.80	20.75	23.90	28.99	31.42
45	25.70	19.38	22.39	26.54	29.15
75	23.72	18.80	21.68	24.50	26.98
135	22.56	18.67	21.60	23.12	24.99
195	22.15	18.58	21.57	22.68	24.80
255	21.74	18.48	21.23	21.23	23.99

T = 15°C

Time Min	Weight of Particles (g)				
	Brine +	Brine + 5 g $CaCl_2$	Brine + 5 g KCl	Brine + 5 g Na_2SO_4	Brine + 25 mL MEOH
0	32.15	31.73	31.92	32.50	32.15
15	26.97	28.84	29.24	28.29	30.12
45	23.75	27.03	26.13	26.36	27.71
75	22.56	25.05	25.17	24.26	26.92
135	22.10	23.99	23.88	23.48	25.06
195	21.94	23.13	23.24	22.51	23.69
255	20.35	22.86	23.01	21.91	23.13

Table 14 - Kinetics of IMC Potash in Brine + Suppressants at 35°C

14a - High Amount of Suppressant

Time Min	Weight of Particles (g)				
	Brine +	Brine + 30 g $CaCl_2$	Brine + 30 g KCl	Brine + 30 g Na_2SO_4	Brine + 75 mL MEOH
0	32.98	34.85	33.75	31.20	31.50
15	26.89	33.86	33.74	29.67	30.95
45	24.86	32.46	33.50	27.78	29.91
75	23.35	30.22	33.49	26.47	28.60
135	22.62	29.44	33.42	25.79	28.00
195	22.45	28.17	32.96	25.64	26.52
255	22.43	26.77	32.54	24.84	25.33

14b - Low Amount of Suppressant

Time Min	Weight of Particles (g)				
	Brine +	Brine + 5 g $CaCl_2$	Brine + 5 g KCl	Brine + 5 g Na_2SO_4	Brine + 25 mL MEOH
0	32.98	32.30	32.24	31.78	31.58
15	26.89	27.72	28.18	27.90	27.63
45	24.86	25.03	25.10	24.61	25.48
75	23.35	23.02	24.83	21.95	23.20
135	22.62	21.39	23.64	20.62	21.52
195	22.45	20.41	23.37	20.00	20.25
255	22.43	20.12	22.89	20.00	20.16

Table 15 - Kinetics of IMC Potash in Brine + Suppressants at 45°C

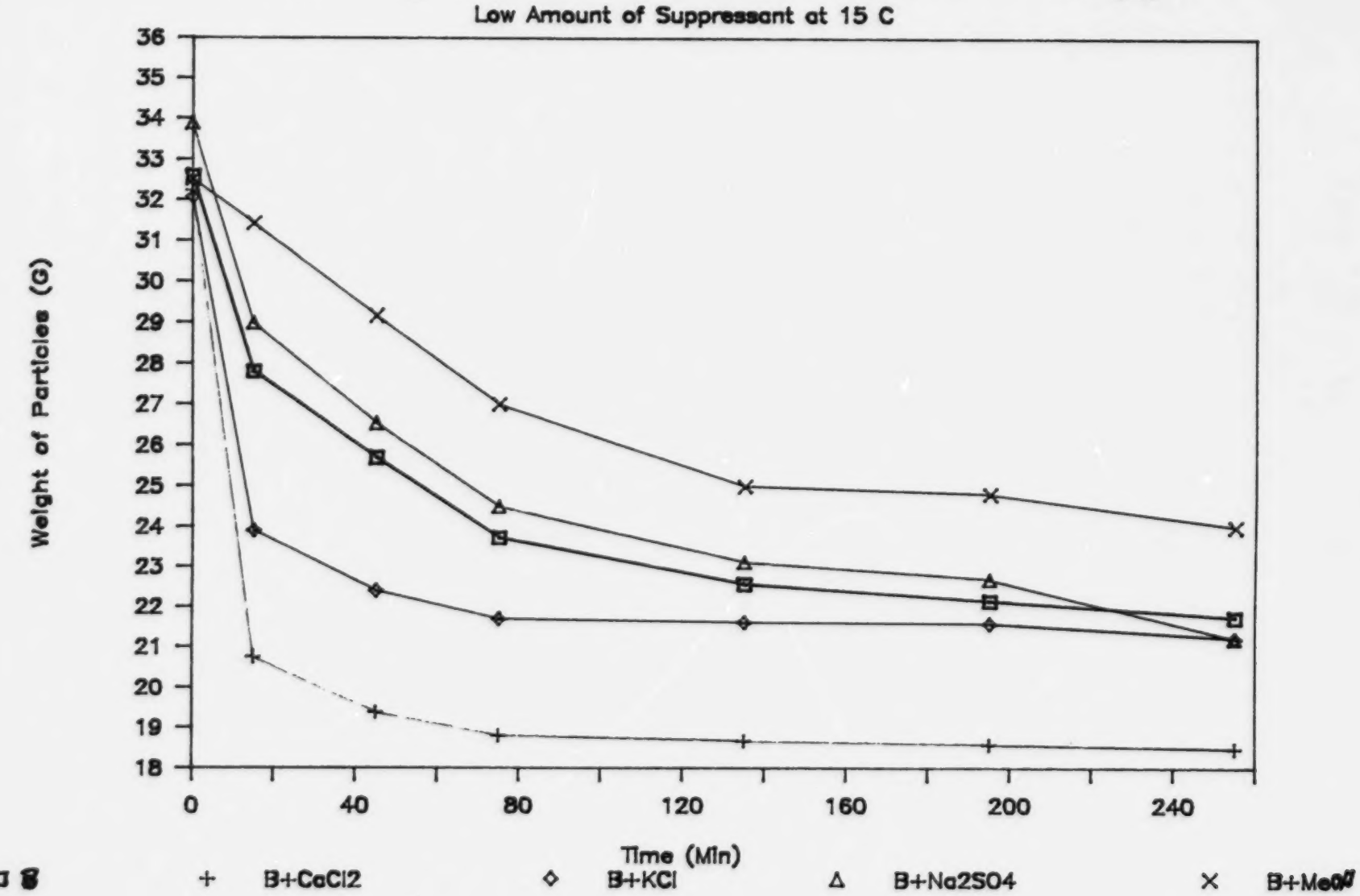
15a - High Amount of Suppressant

Time Min	Weight of Particles (g)				
	Brine +	Brine + 30 g $CaCl_2$	Brine + 30 g KCl	Brine + 30 g Na_2SO_4	Brine + 75 mL MEOH
0	31.56	35.0	35.47	32.32	33.37
15	25.74	33.59	34.83	30.06	31.55
45	23.32	30.47	33.65	29.54	29.54
75	23.28	29.42	33.35	27.50	29.04
135	23.17	29.95	33.18	27.43	27.37
195	23.08	27.38	32.74	26.06	26.10
255	23.23	25.15	32.58	25.96	25.86

15b - Low Amount of Suppressant

Time Min	Weight of Particles (g)				
	Brine +	Brine + 5 g $CaCl_2$	Brine + 5 g KCl	Brine + 5 g Na_2SO_4	Brine + 25 mL MEOH
0	31.56	31.43	32.49	31.96	31.62
15	25.74	29.28	30.20	26.53	28.46
45	23.32	27.20	28.10	24.67	25.78
75	23.28	25.05	25.94	22.34	23.39
135	23.17	23.73	25.00	21.84	23.23
195	23.08	22.74	24.83	21.82	22.99
255	23.23	21.52	24.34	21.80	22.09

Figure 34 - *Kinetics of IMC Potash in Brine + Suppr*



the suppressants are effective even at low concentrations (Figure 35). At the higher temperatures of 35 and 45°C, the effect of low amounts of suppressant is very insignificant and quite close (Figures 36 and 37). At higher amounts of suppressants and the high temperatures of 35 and 45°C, the trend is very clear as shown in Figures 38 and 39. Suppressants in decreasing order of effectiveness are:

$$KCl > CaCl_2 > Methanol > Na_2SO_4$$

The equilibrium is achieved faster at high temperatures. At 45°C, equilibrium for brine and for brine + KCl were achieved within 45 minutes, while at 35°C equilibrium was reached at 75 minutes.

For many reactions, the rate expression can be written as a product of a temperature-dependent term and a composition-dependent term, or

$$r = K.\ f\ (composition) \qquad (18)$$

The reaction rate constant, has been found to be well represented by the Arrhenius' law:

$$K = K.e^{-E/RT} \qquad (19)$$

where K. = frequency factor

E = activation energy

T = Temperature

R = constant

From the above formula, the rate constant should increase with temperature and as a result, the rate of dissolution or rate of reaction should increase with temperature as well. However, there is another factor that is operating in this process and that is the rate of mass transfer. Diffusion of particles through the ash (precipitate) layer yields another resistance to the overall rate.

The rate-controlling step of a fluid-solid reaction is deduced by noting how the progressive conversion of particles is influenced by particle size and

Figure 35 - *Kinetics of IMC Potash in Brine + Suppr*

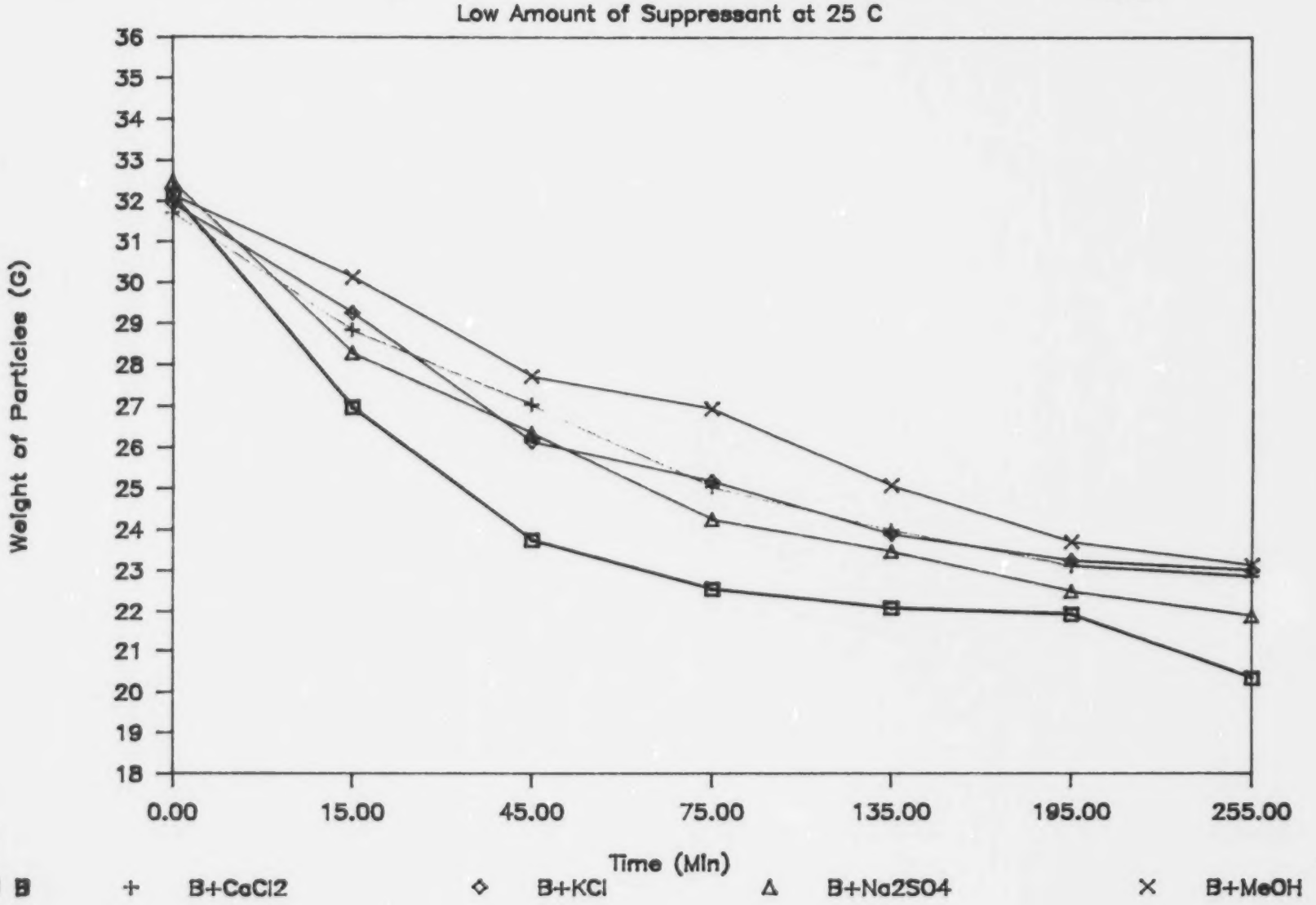


Figure 36 - *Kinetics of IMC Potash in Brine + Suppr*

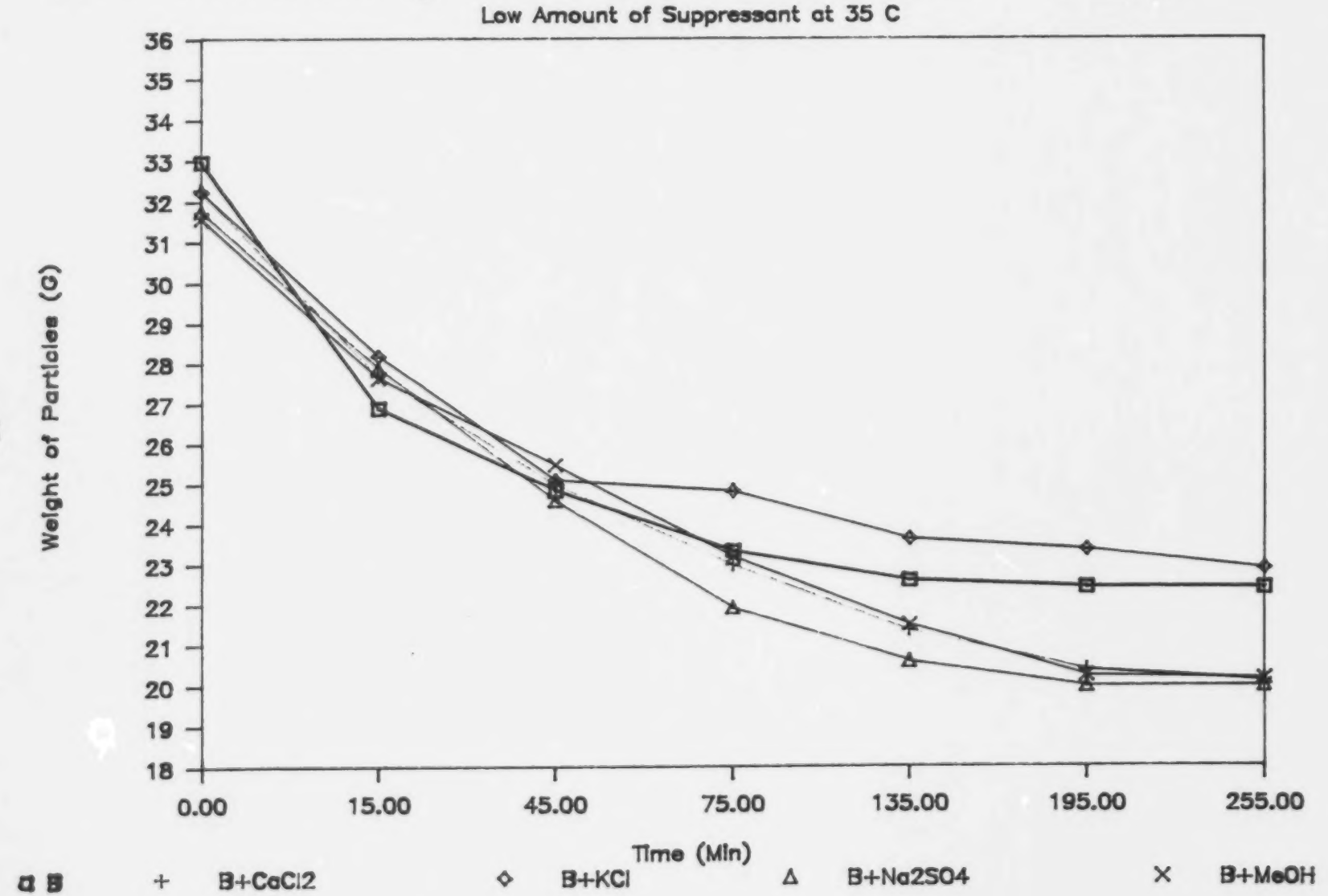


Figure 37 - *Kinetics of IMC Potash in Brine + Suppr*

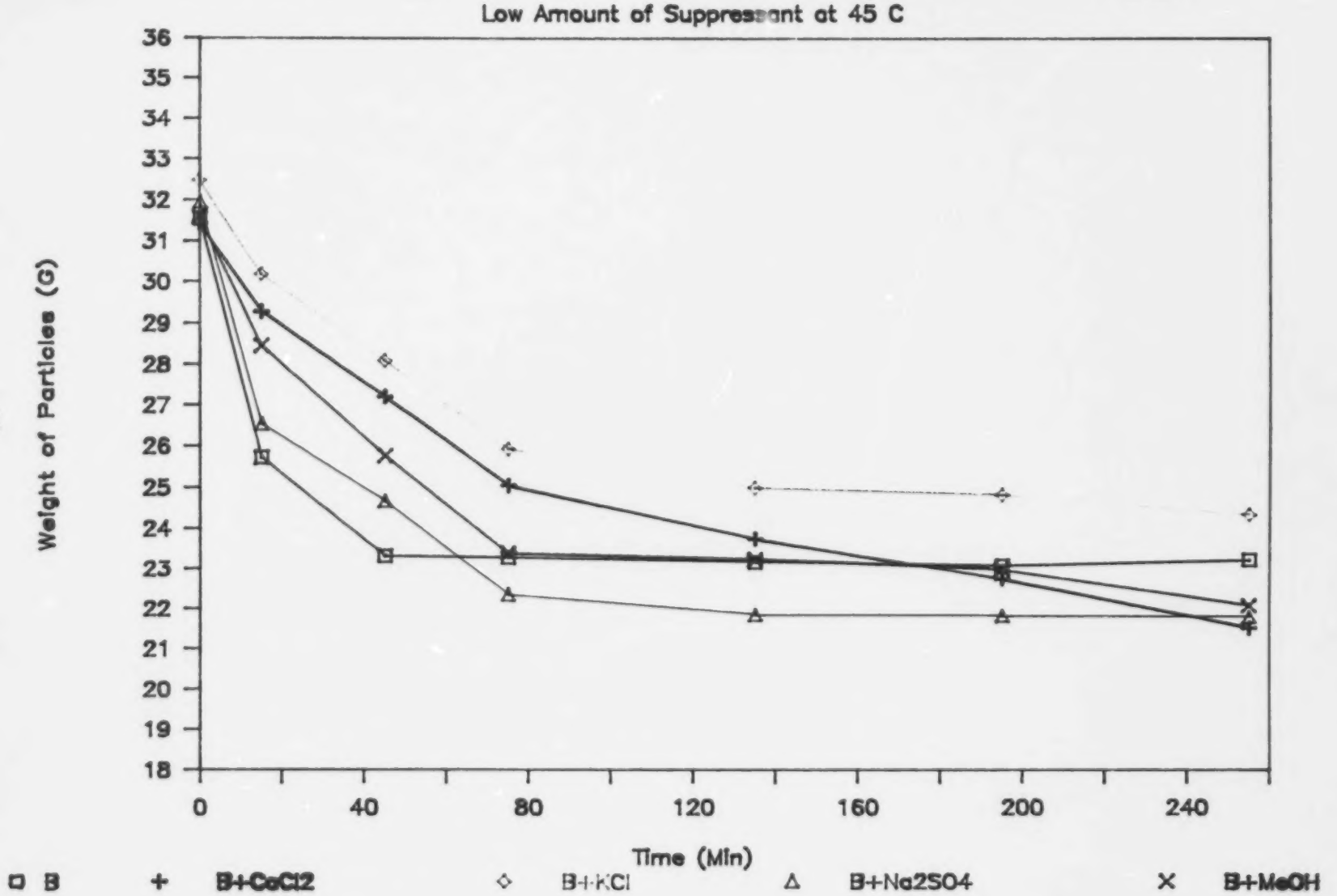


Figure 38 - *Kinetics of IMC Potash in Brine +Suppr*

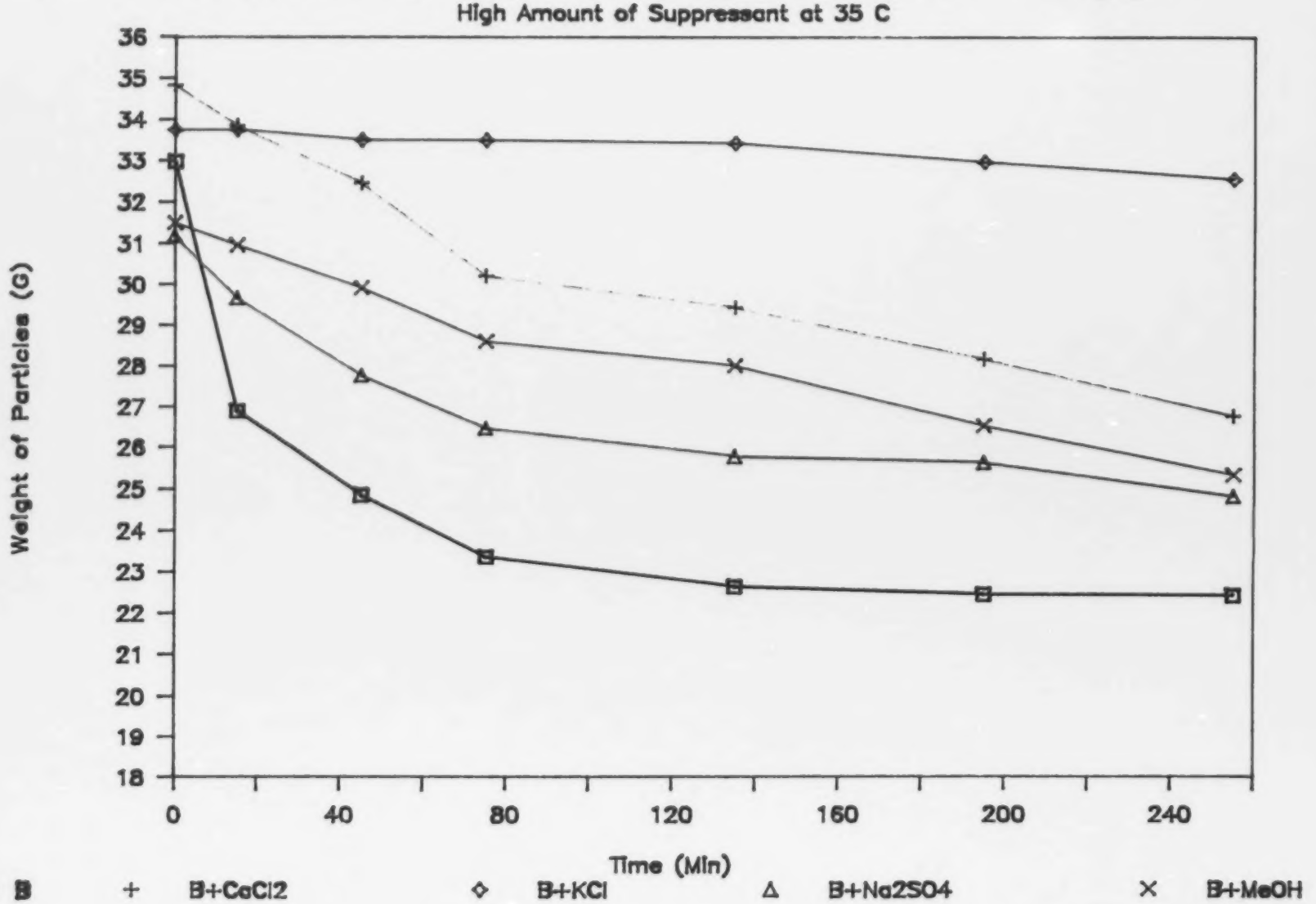
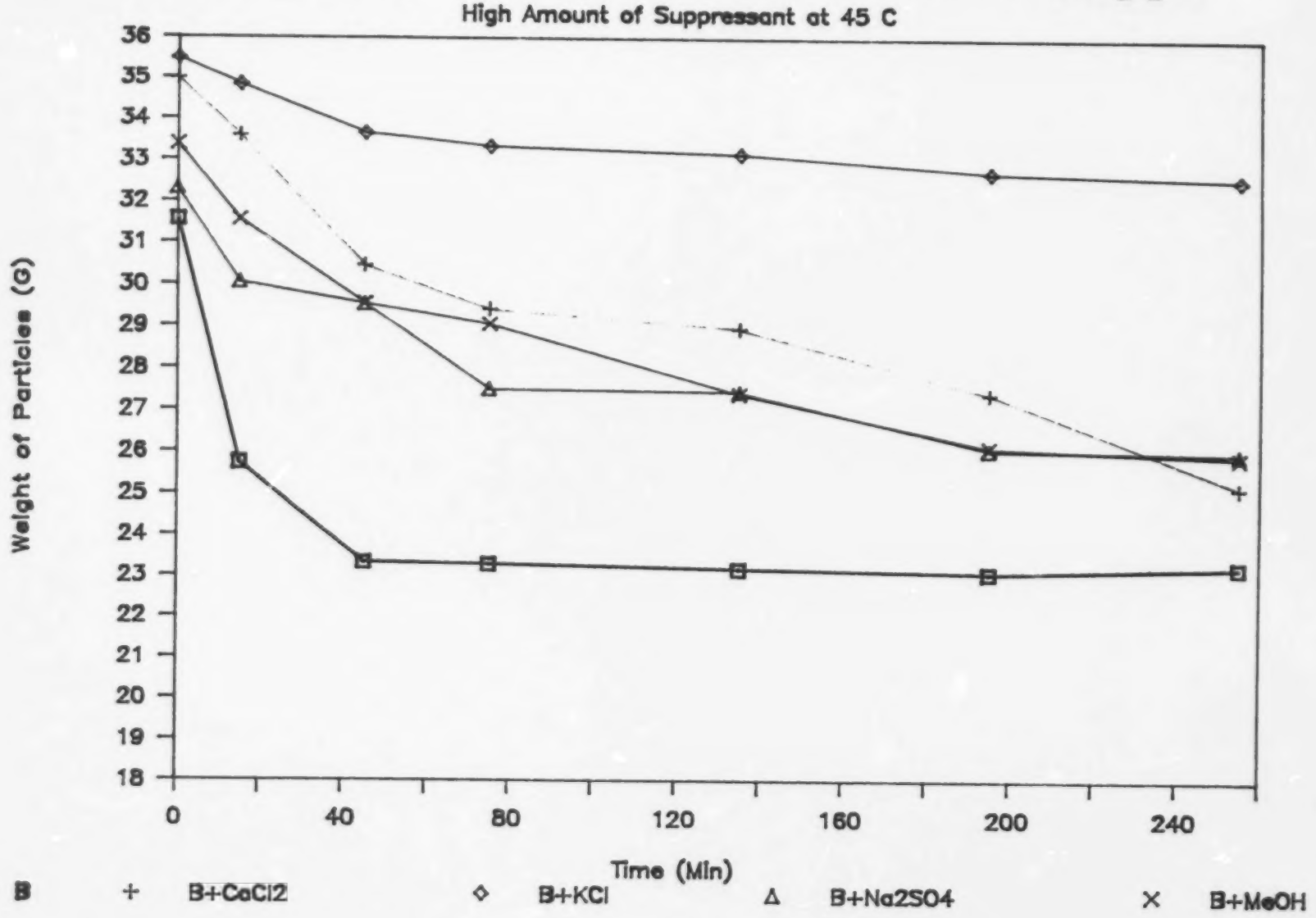


Figure 39 - *Kinetics of IMC Potash in Brine + Suppr*



operating temperature. The chemical step is usually much more temperature-sensitive than the physical steps. Hence, experiments at different temperatures should easily distinguish between ash or film diffusion on one hand and chemical reaction on the other hand as the controlling step. Figure 32 shows the effect of temperature on the rate of dissolution of particles in brine. This figure shows that the rate is not very temperature sensitive. We could conclude, therefore, that the main resistance to reaction is the diffusion through the ash layer surrounding the particles and not the reaction step.

5.1c Static Test at 25°C and Different Mixing Speed

In the static test, the vessels containing the reactants were held in the water bath shaker. In this set of experiments, the affect of change in speed of the shaker on the rate of dissolution was verified. The data is tabulated in Tables 16, 17 and 18.

At a low speed of mixing, dissolution of the particles is a slow process (Figures 40 and 41). At higher speeds, it becomes like an instantaneous dissolution over a very short period of time (Figure 42). Low concentrations of suppressants at high speed had no affect on the dissolution rate. At higher speeds with high concentrations of the suppressant KCl a significant affect was observed and with $CaCl_2$ a moderate affect on the rate of dissolution was observed (Figures 43 and 44).

At the low speed of mixing, the rate of dissolution is very gradual (Figure 41) for all the suppressants. At higher speeds, for the same suppressants, the rate of dissolution increased significantly (Figure 43). We could, therefore, conclude that at high mixing rates, the resistance due to diffusion through the ash layer is reduced and the rate of reaction becomes the controlling step (except in KCl). At lower mixing rates, both chemical reaction

Table 16 - Kinetics of IMC Potash in Brine + Suppressants at 25°C and Mixing Speed of 170 RPM

Time Min	Weight of Particles (g)				
	Brine +	Brine + $CaCl_2$ (20 G)	Brine + 30 g KCl	Brine + 30 g Na_2SO_4	Brine + 75 mL MEOH
0	32.15	32.57	32.25	32.98	32.49
15	26.97	32.57	31.90	28.54	31.09
45	23.75	30.01	31.99	26.18	29.43
75	22.56	28.11	31.97	24.84	28.24
135	22.10	27.00	31.98	24.86	28.20
195	21.64	25.99	31.89	24.04	27.44
255	20.35	24.90	31.95	23.56	26.33

Table 17 - Kinetics of IMC Potash in Brine + Suppressants at 25°C and Different Mixing Speeds

17a - (speed 7 = 260 RPM)

Time Min	Weight of Particles (g)				
	Brine +	Brine + 30 g $CaCl_2$	Brine + 30 g KCl	Brine + 30 g Na_2SO_4	Brine + 75 mL MEOH
0	32.31	34.25	34.18	32.73	31.23
15	23.22	26.45	32.28	20.74	29.37
45	22.35	22.48	32.14	20.71	24.85
75	22.40	21.48	32.10	20.57	22.31
135	22.71	20.57	32.00	20.39	21.38
195	22.11	20.53	31.76	20.07	20.65
255	21.89	20.17	31.52	19.64	20.00

17b - (speed 9 = 350 RPM)

Time Min	Weight of Particles (g)				
	Brine +	Brine + 30 g $CaCl_2$	Brine + 20 g KCl	Brine + 30 g Na_2SO_4	Brine + 75 mL MEOH
0	32.82	35.00	33.16	32.60	31.81
15	22.26	25.59	32.36	21.00	25.05
45	21.72	24.26	31.79	20.81	21.70
75	21.04	23.94	31.57	20.64	20.37
135	20.75	22.79	31.39	20.58	19.70
195	20.65	22.66	31.35	20.55	19.46
255	20.64	22.46	30.85	20.53	19.26

Table 18 - Kinetics of IMC Potash in Brine + Suppressants at 25°C and Different Mixing Speeds

Speed 7 = 260 RPM

Time Min	Weight of Particles (g)				
	Brine +	Brine + 5 g $CaCl_2$	Brine + 5 g KCl	Brine + 5 g Na_2SO_4	Brine + 25 mL MEOH
0	32.31	32.24	32.06	32.70	31.63
15	23.22	20.75	23.90	20.83	23.13
45	22.35	19.38	22.39	20.69	19.87
75	22.40	18.80	21.68	20.32	19.46
135	22.71	18.67	21.60	20.23	19.08
195	22.11	18.58	21.57	20.07	19.00
255	21.89	18.48	21.23	19.91	18.69

Speed 5 = 170 RPM

Time Min	Weight of Particles (g)				
	Brine +	Brine + 5 g $CaCl_2$	Brine + 5 g KCl	Brine + 5 g Na_2SO_4	Brine + 25 mL MEOH
0	32.15	31.73	31.92	32.50	32.15
15	26.97	28.84	29.24	28.29	30.12
45	23.75	27.03	26.13	26.36	27.71
75	22.56	25.05	25.17	24.26	26.92
135	22.10	23.99	23.88	23.48	25.06
195	21.94	23.13	23.24	22.51	23.69
255	20.35	22.86	23.01	21.91	23.13

Figure 40 - *Kinetics of IMC Potash in Brine + Suppr*

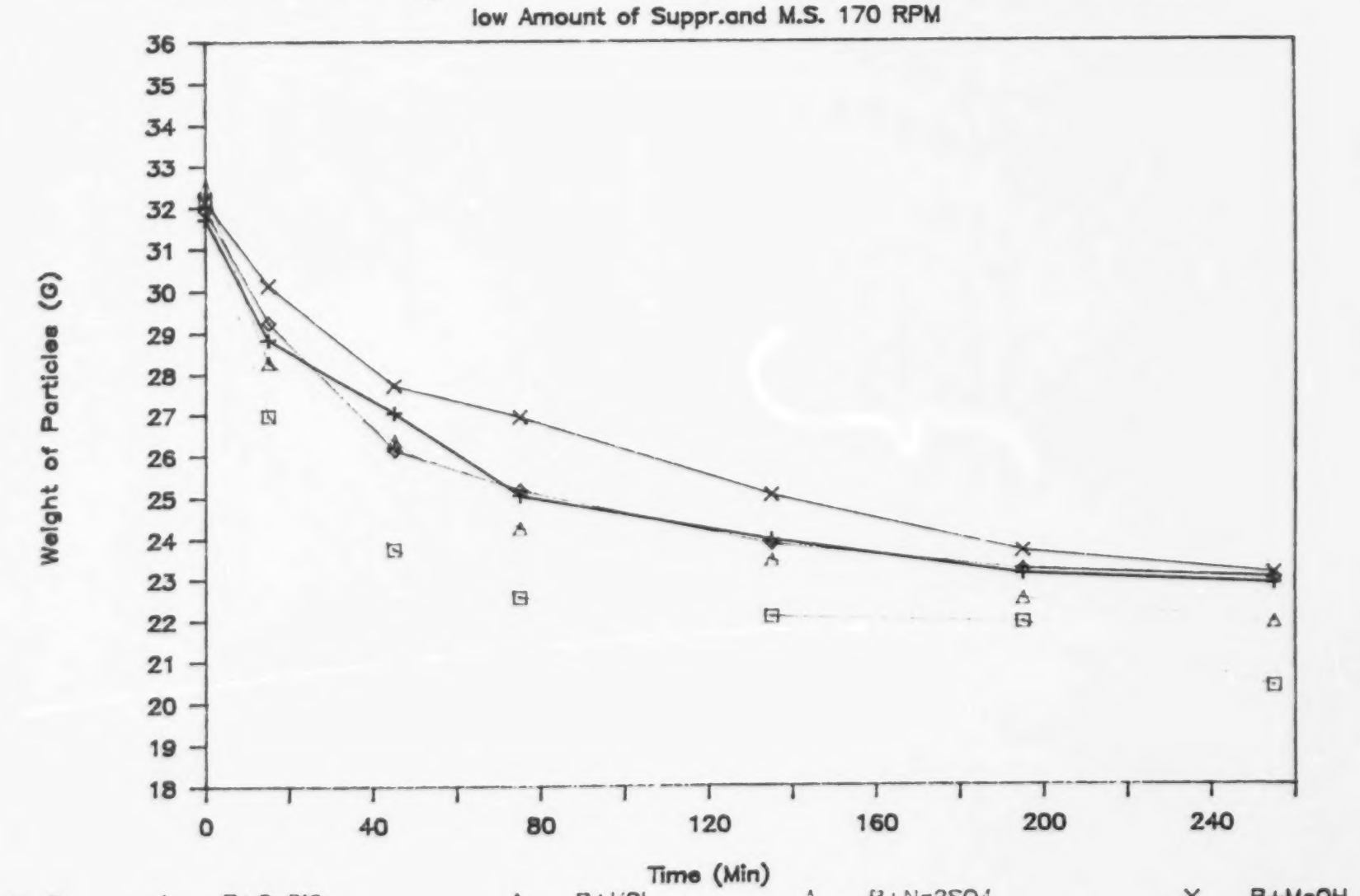


Figure 41 - *Kinetics of IMC Potash in Brine + Suppr*

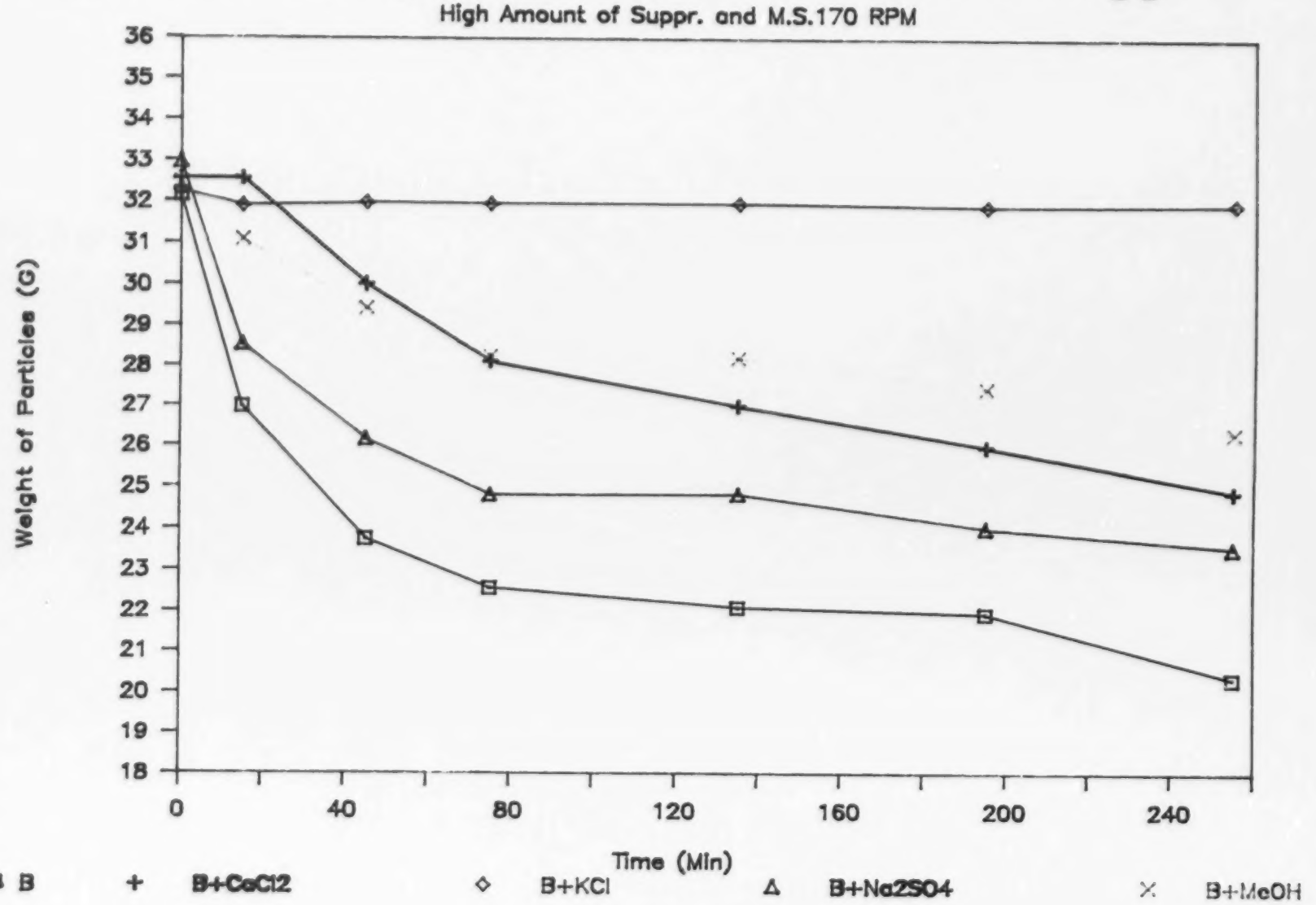


Figure 42 - *Kinetics of IMC Potash in Brine + Suppr*

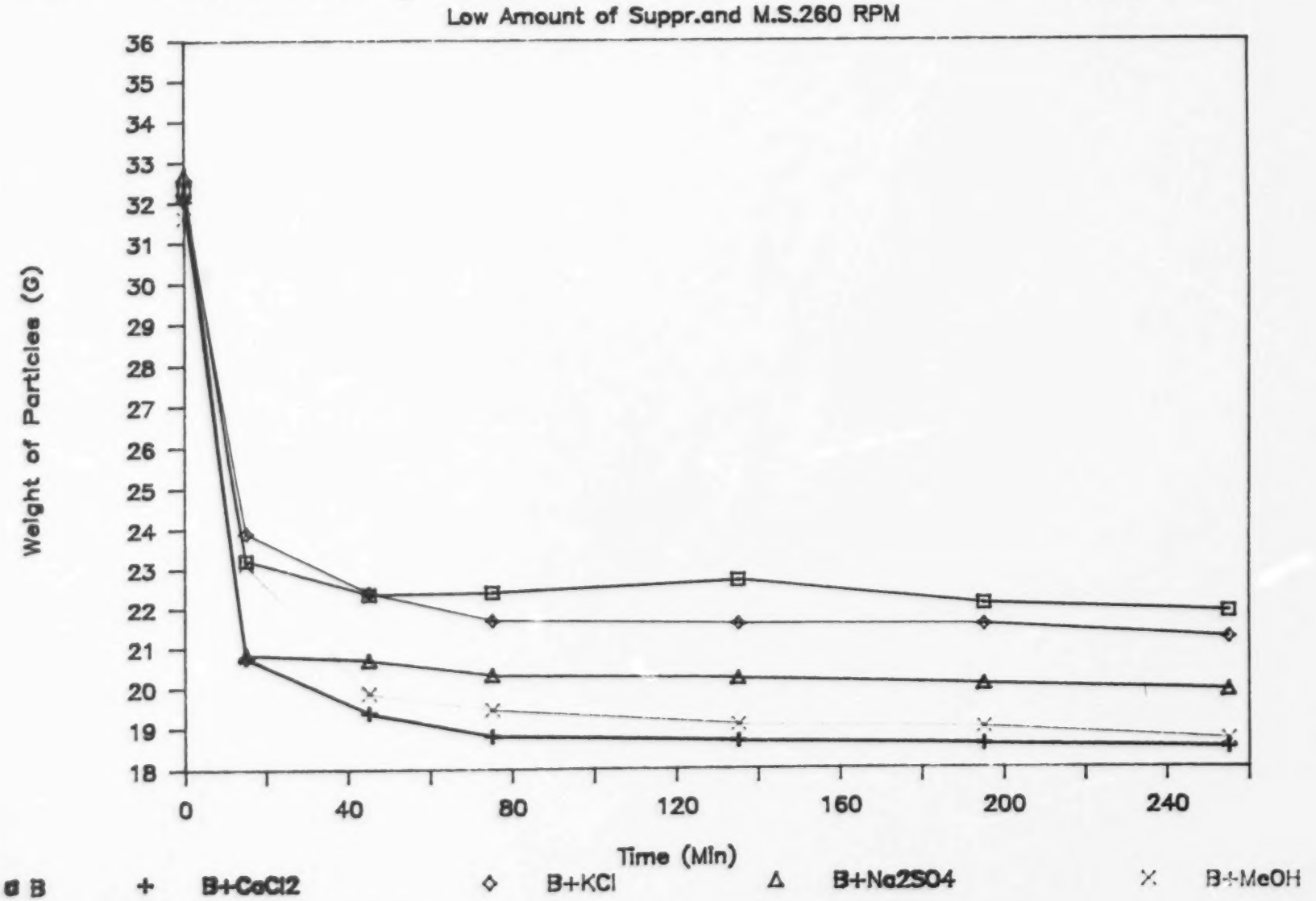


Figure 43 - *Kinetics of IMC Potash in Brine +Suppr*

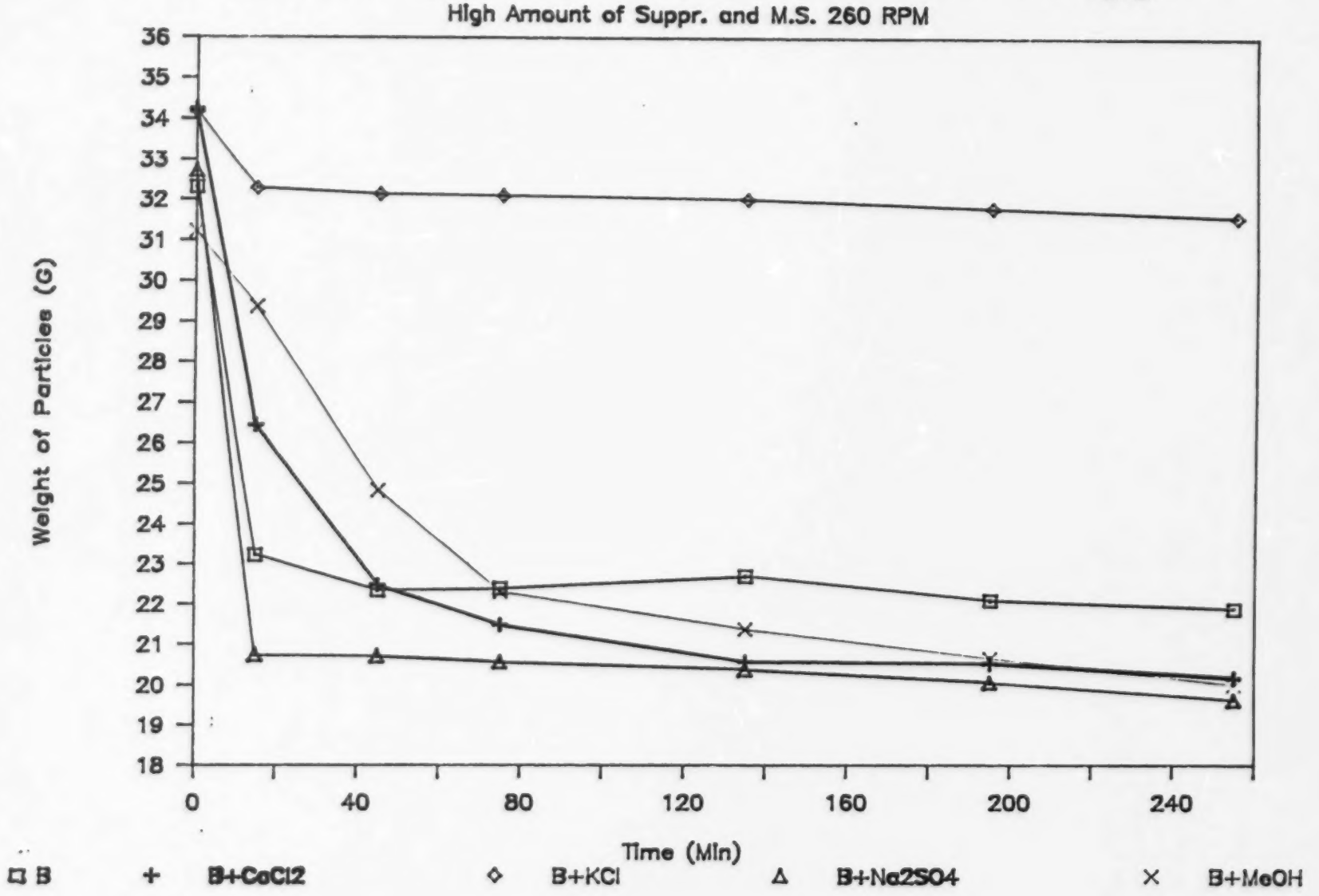
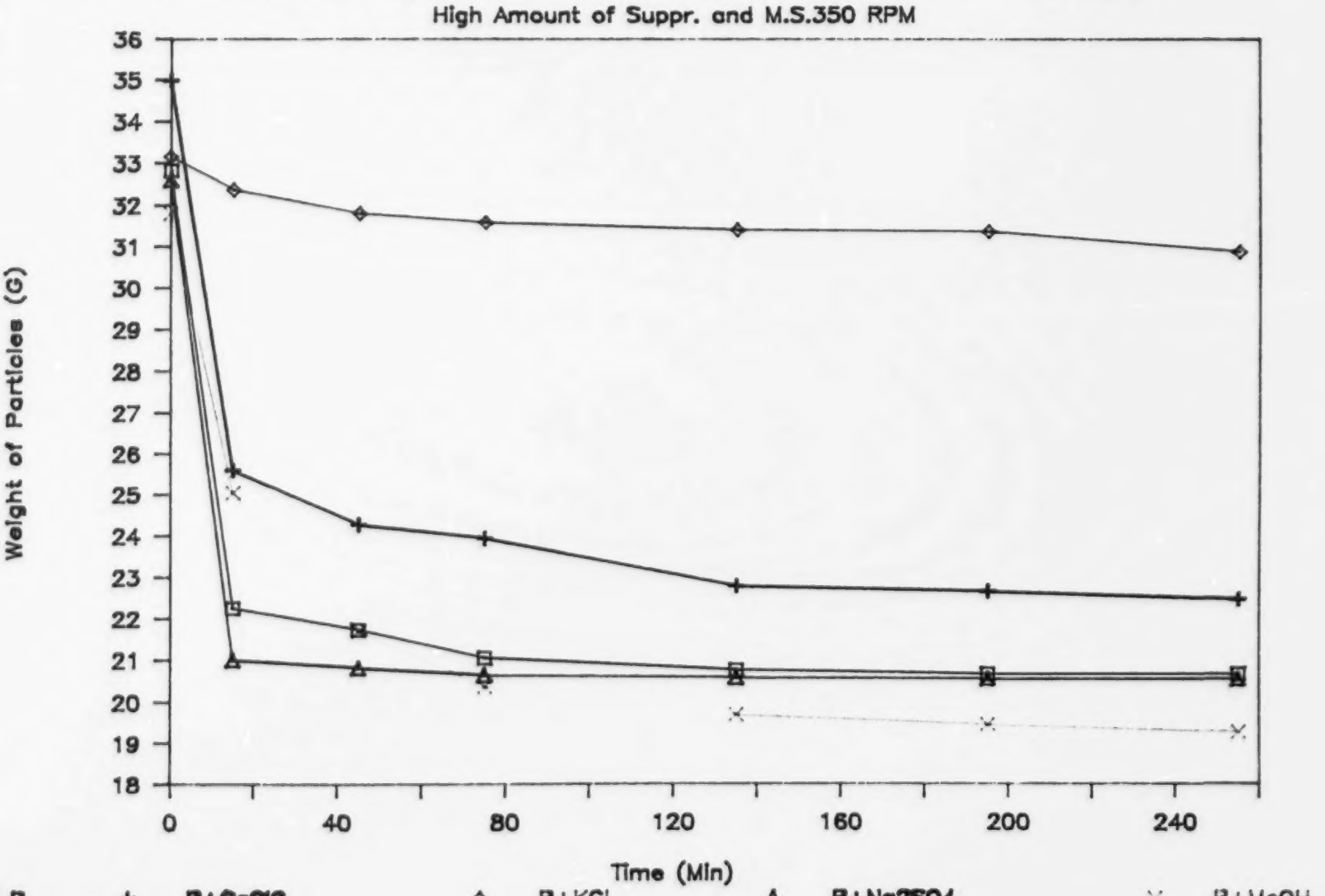


Figure 44 - *Kinetics of IMC Potash in Brine +Suppr*



step and diffusion step are controlling steps.

5.1d Kinetic Studies

To study the order of reaction by the Integral Method (Section 3.2), we assumed a first order reversible reaction. Equation 16 was then used. The $\ln[(1 + k_2/k_1)\ X - k_2/k_1]$ versus time was drawn and the linearity of data was checked. Figures 45, 46 and 47 show the graph for CCP red, CCP white and IMC brine without any suppressant. The graphs show some linearity, indicating that in case of brine samples alone, rate of reaction could be controlling because of the absence of ash layer at least at the beginning of the experiments. IMC data (Figure 47) shows the same trend.

In the case of brine and suppressant experiments, the precipitate form an ash layer on the particles and gradually diffusion through the layer becomes rate-controlling. In case of $CaCl_2$ and methanol, the particles remain in colloidal form. The formation of the ash layer on the particles could or could not be the rate-controlling step. The data was therefore checked with Equation 16 for verification. Figures 48, 49 and 50 show the data fitting for the 5, 10 and 20 g of $CaCl_2$. Figures 51 and 52 indicate the value of the rate constants k_1 and k_2 with respect to the percent of suppressants. The method of calculation were explained in Section 3.2. They do not show any linearity.

The data for methanol as a suppressant was fitted to Equation 16 and are shown graphically in Figures 53, 54 and 55 for CCP brine + 25 mL methanol, CCP + 50 mL methanol and CCP + 75 mL methanol. Some show very linear results. Values of k_1 and k_2 versus percent of suppressant are shown in Figures 56 and 57. Data shows very good linearity.

5.1e CSTR Test

This experiment was carried out with CCP brine and CCP potash lumps, that were identified by letters A to Z. Two types of potash core materials were used.

Figure 45 -

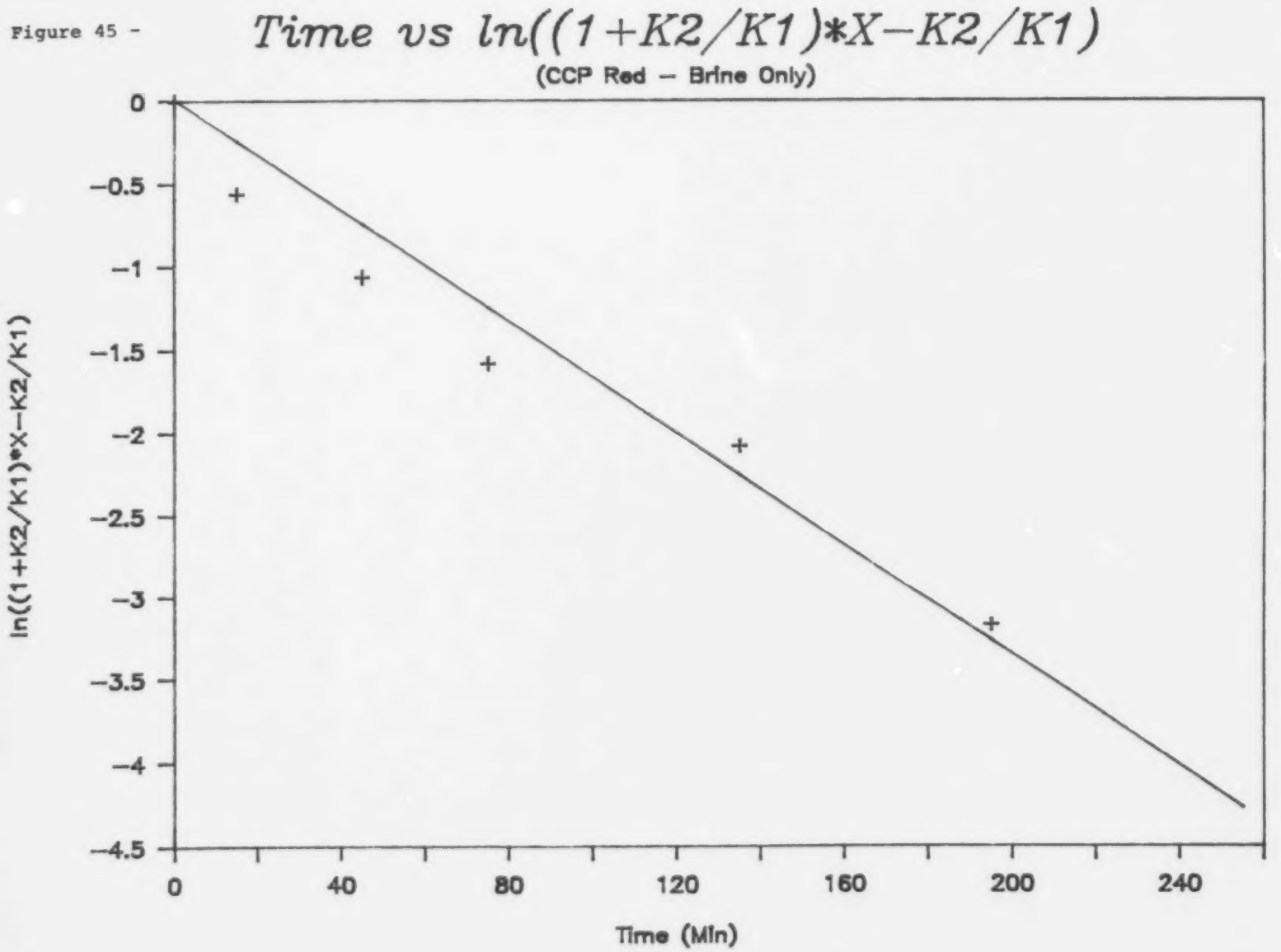

Time vs ln((1+K2/K1)*X-K2/K1)
(CCP Red – Brine Only)
ln((1+K2/K1)*X-K2/K1)
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
0
40
80
120
160
200
240
Time (Min)

Figure 46 - *Time vs ln((1+K2/K1)*X−K2/K1)*

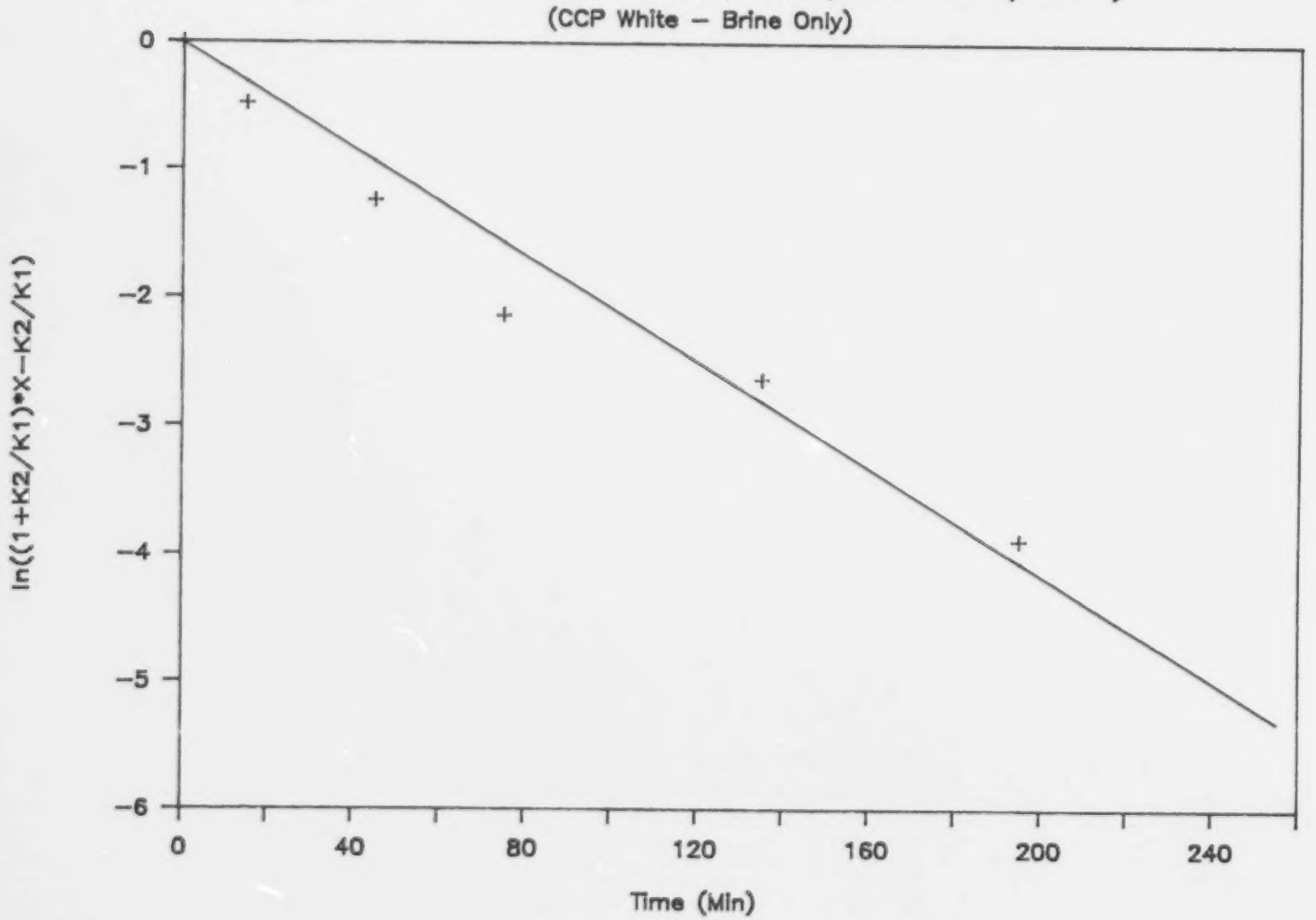


Figure 47 -

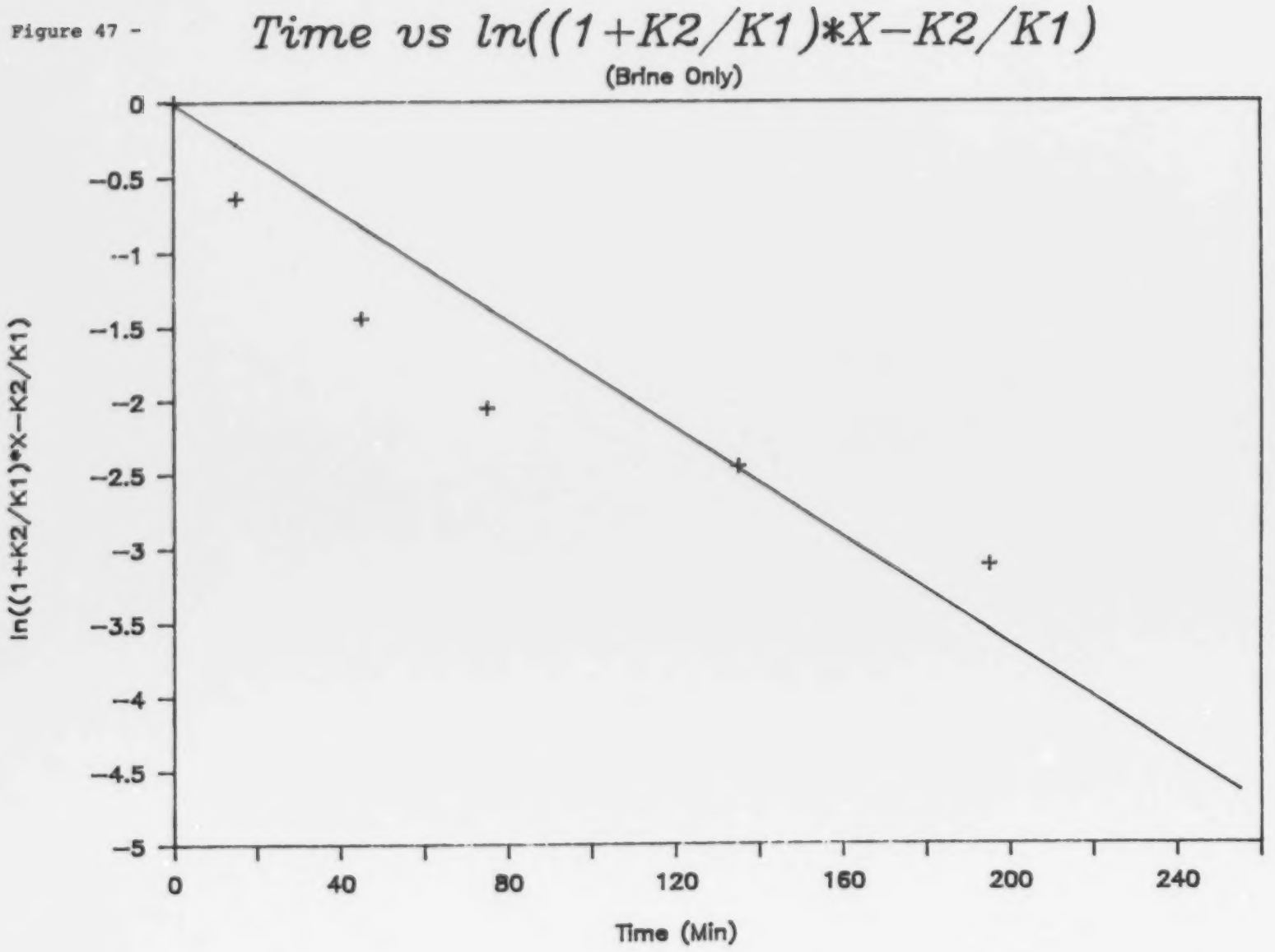

Time vs ln((1+K2/K1)*X-K2/K1)
(Brine Only)
ln((1+K2/K1)*X-K2/K1)
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
0
40
80
120
160
200
240
Time (Min)

Figure 48 - *Time vs ln((1+K2/K1)*X−K2/K1)*

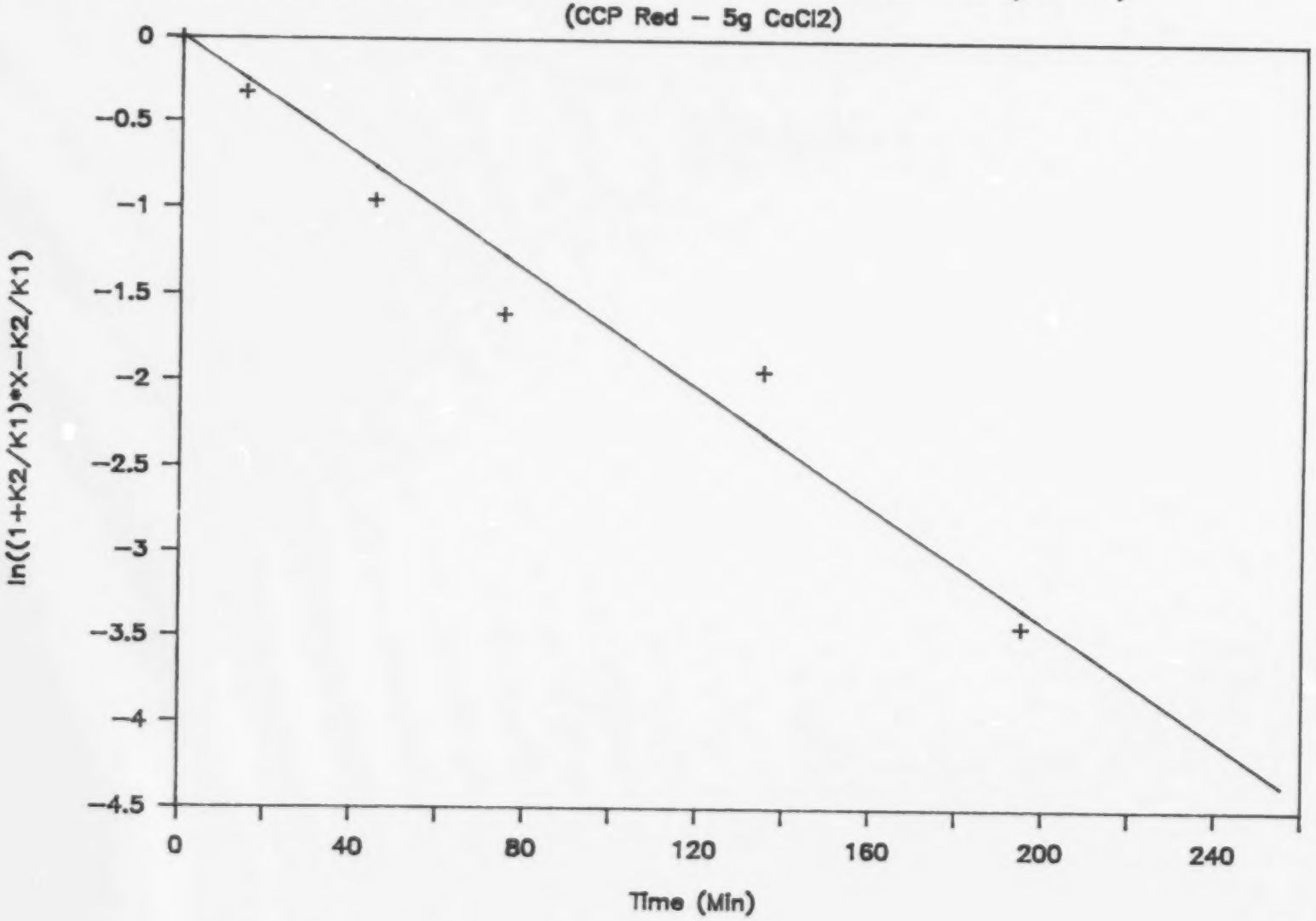


Figure 49 - *Time vs ln((1+K2/K1)*X−K2/K1)*

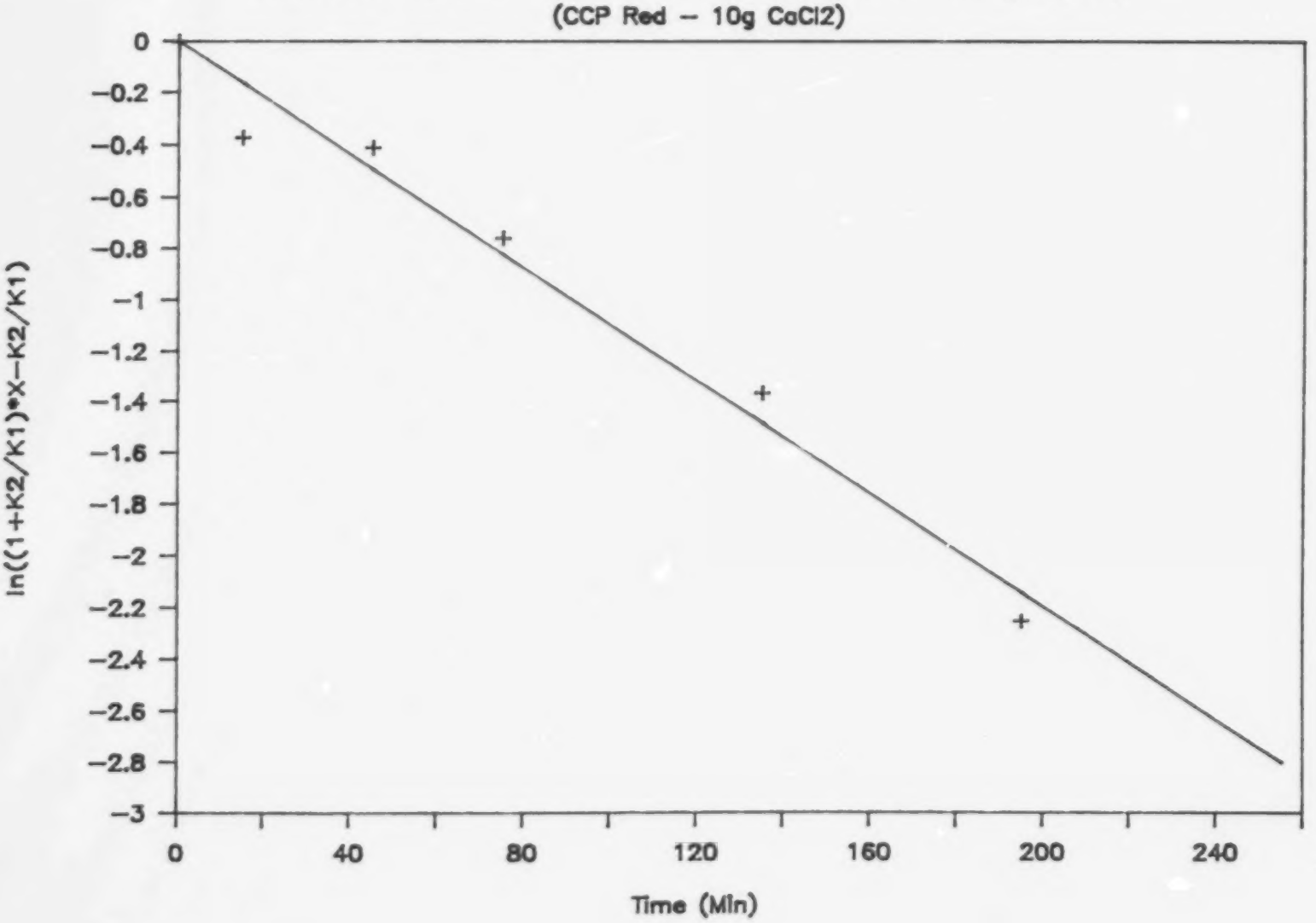


Figure 50 -

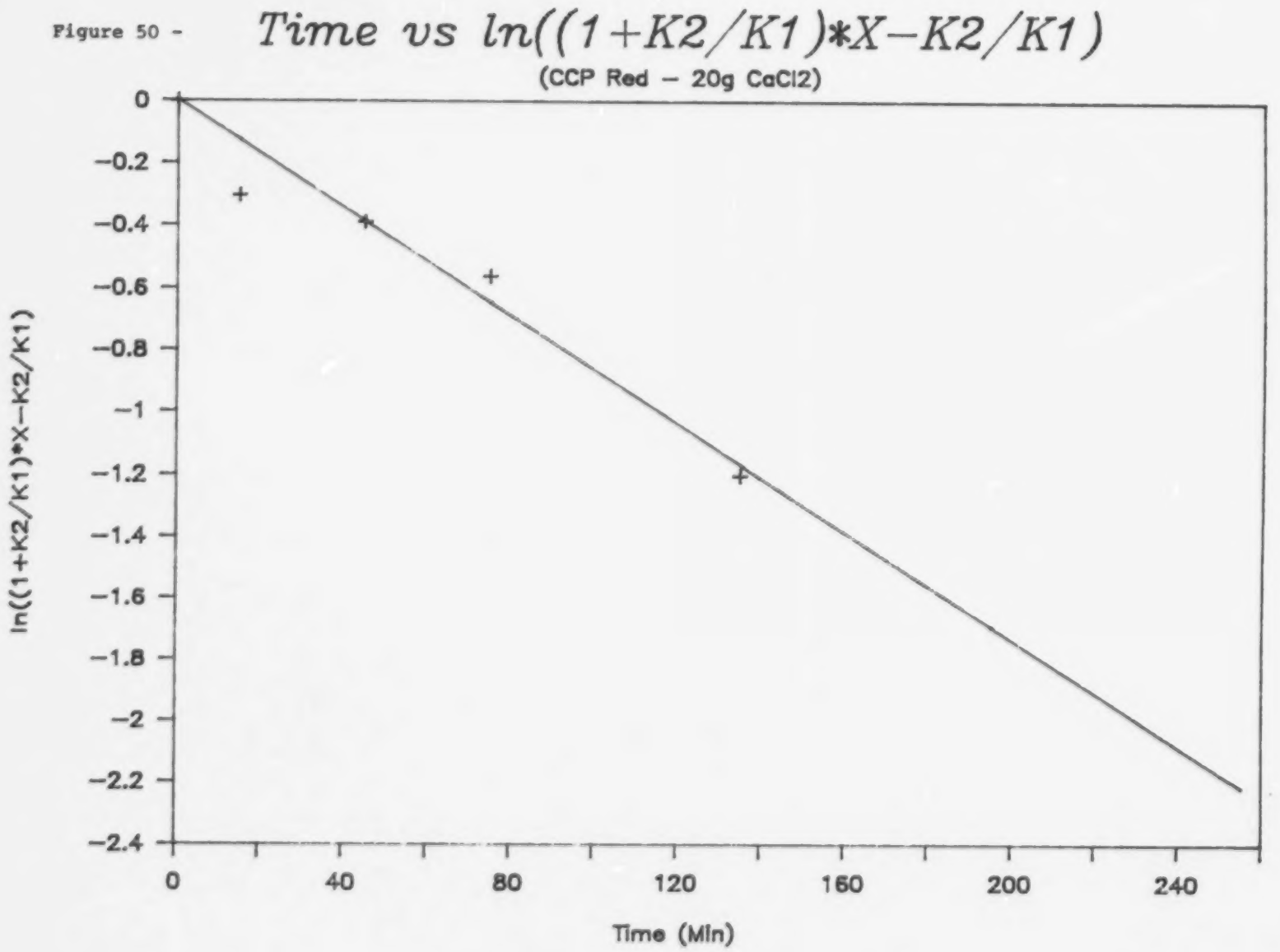

Time vs ln((1+K2/K1)*X-K2/K1)
(CCP Red - 20g CaCl2)
ln((1+K2/K1)*X-K2/K1)
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
-1.8
-2
-2.2
-2.4
0
40
80
120
160
200
240
Time (Min)

Figure 51 - *K1 vs % Suppressant*

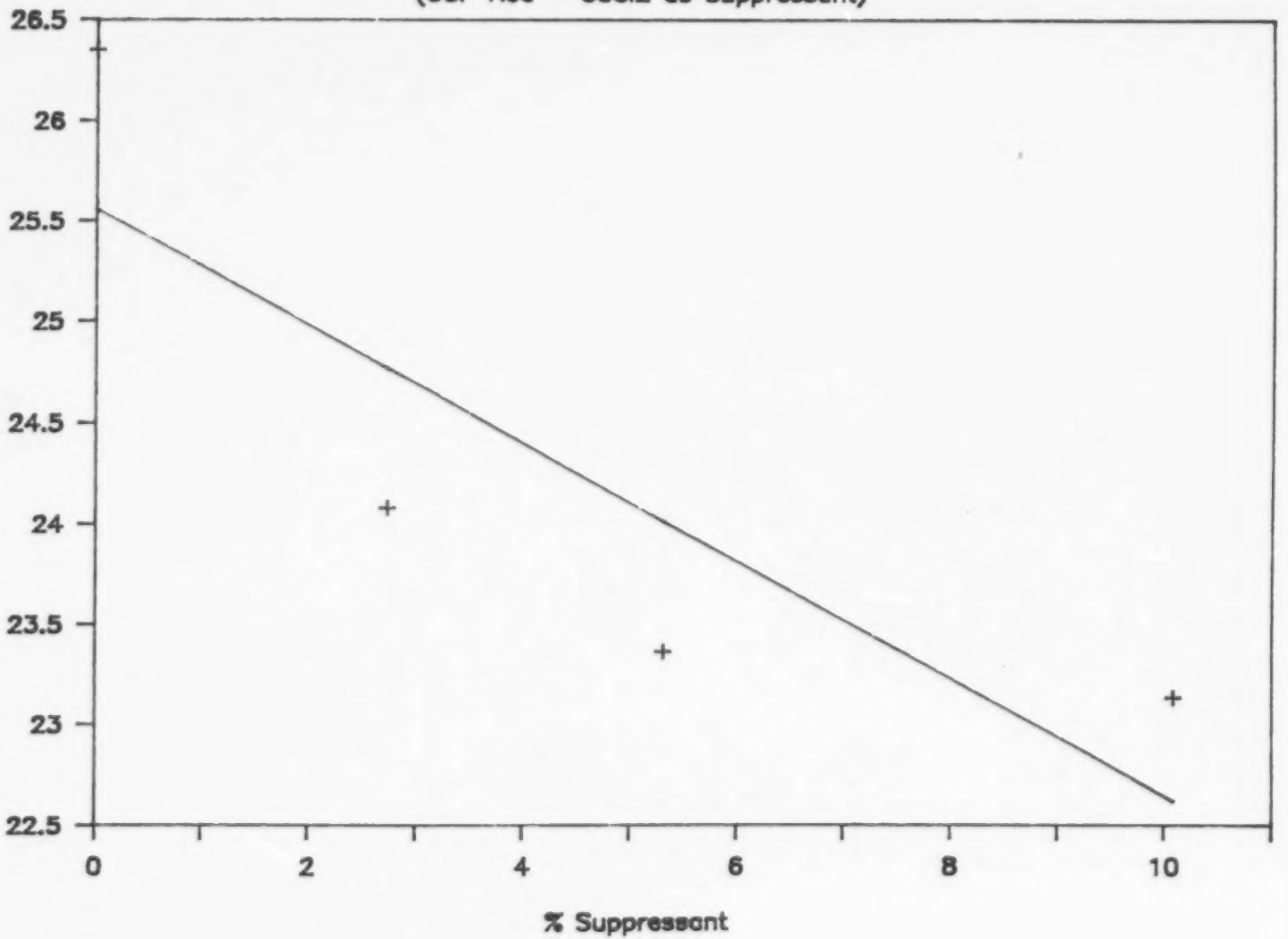


Figure 52 -

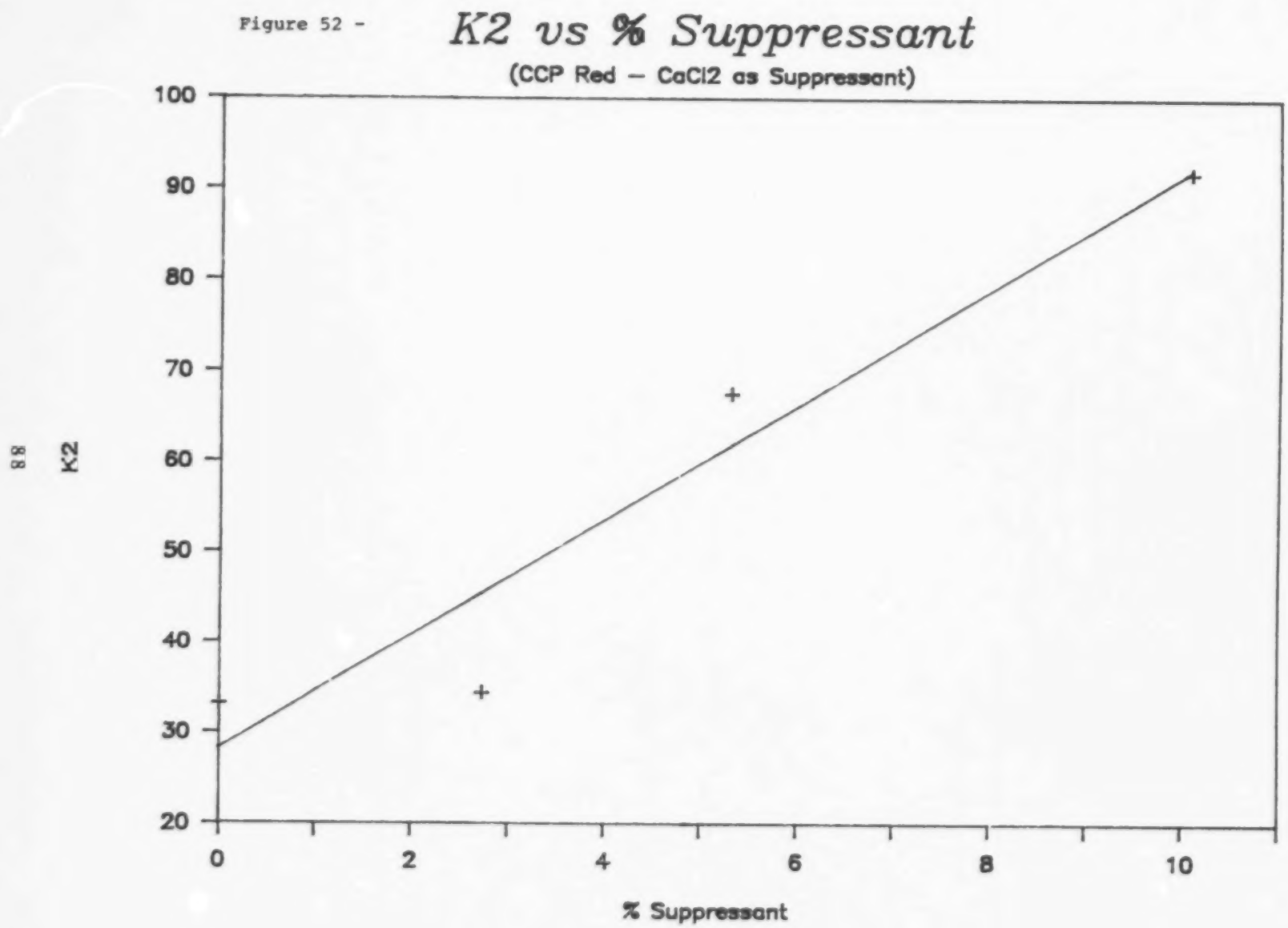

K2 vs % Suppressant
(CCP Red – CaCl2 as Suppressant)
100
90
80
70
60
50
40
30
20
K2
0
2
4
6
8
10
% Suppressant

Figure 53 - *Time vs ln((1+K2/K1)*X−K2/K1)*

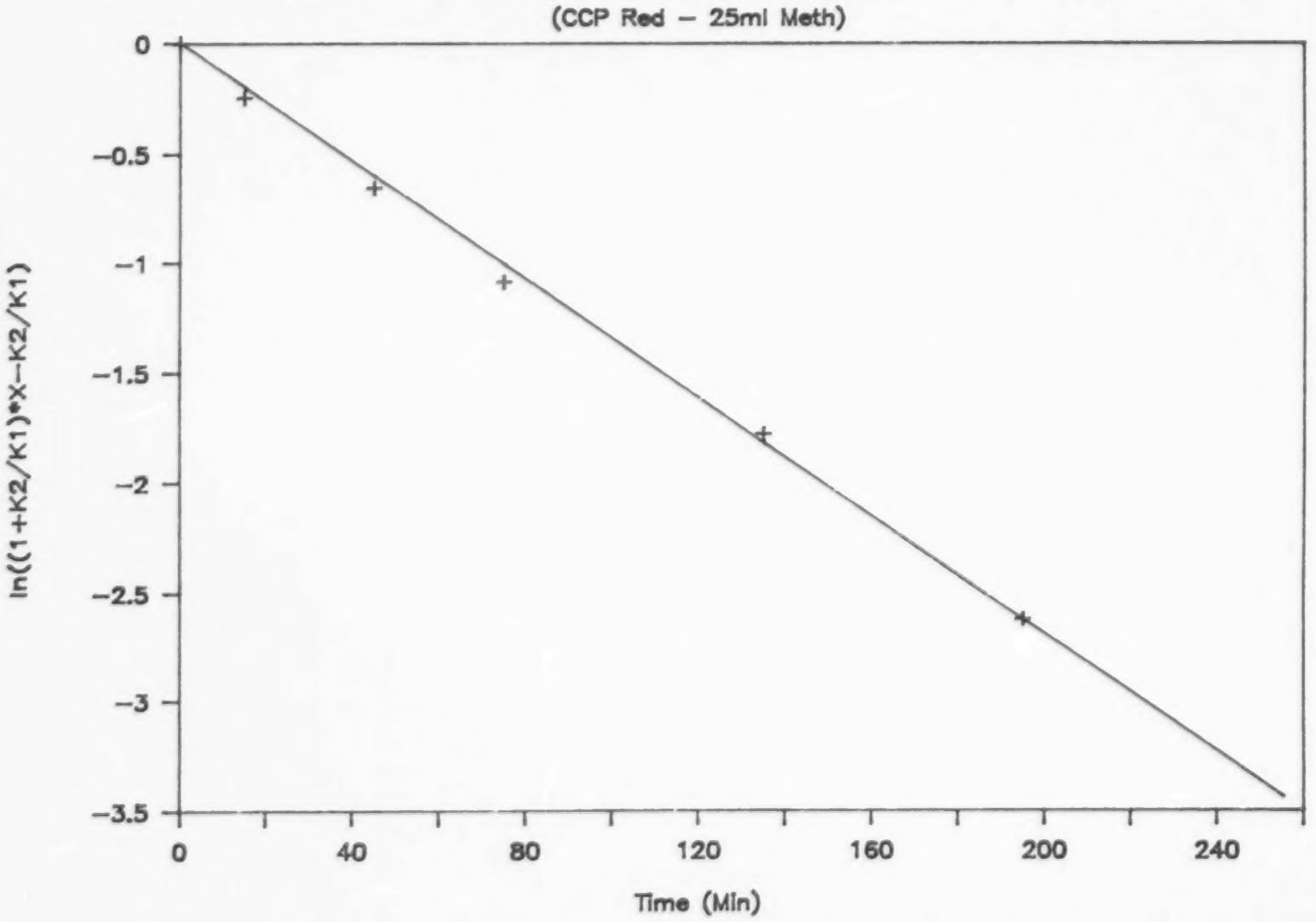


Figure 54 *Time vs ln((1+K2/K1)*X−K2/K1)*

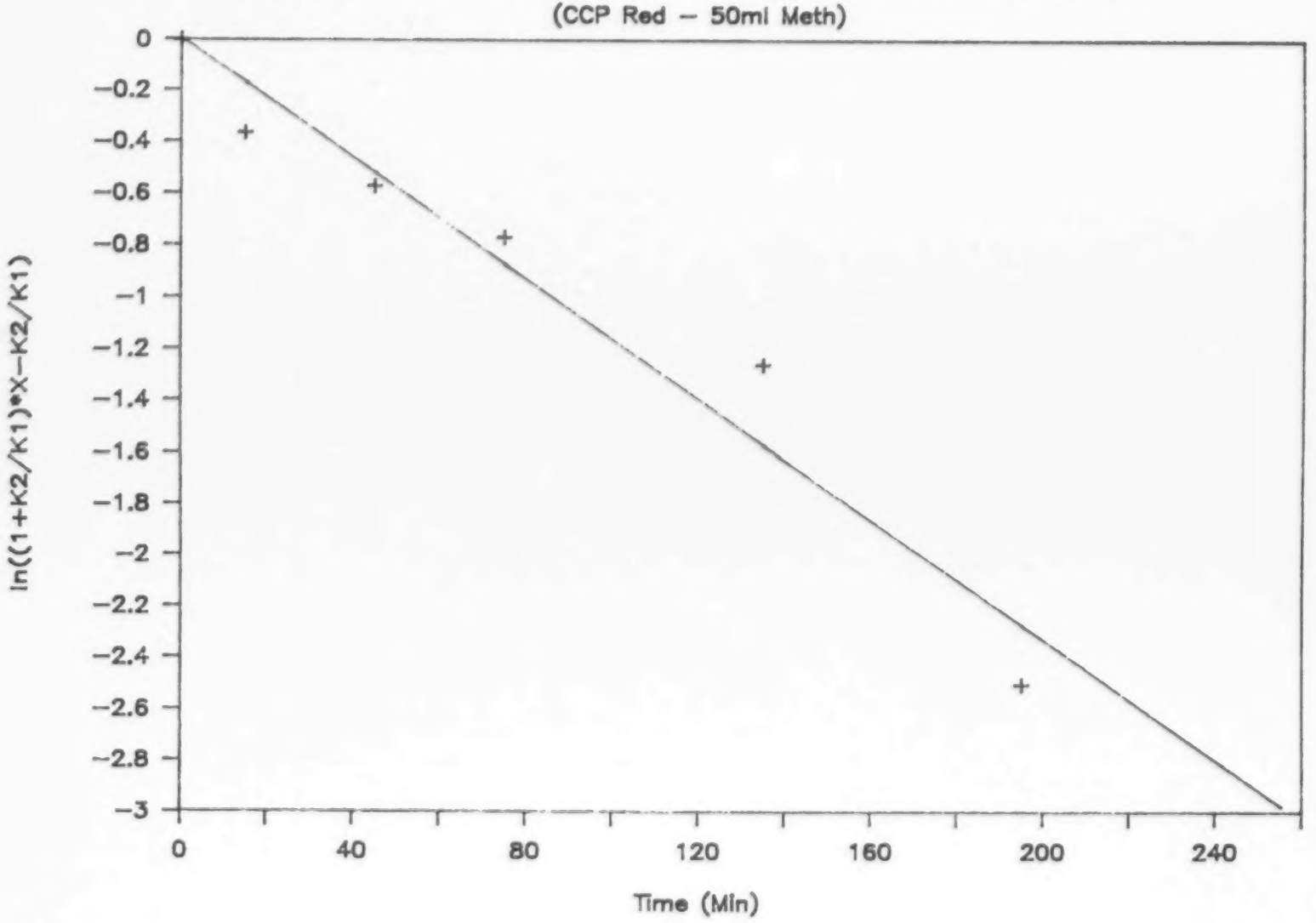


Figure 55 - *Time vs ln((1+K2/K1)*X−K2/K1)*

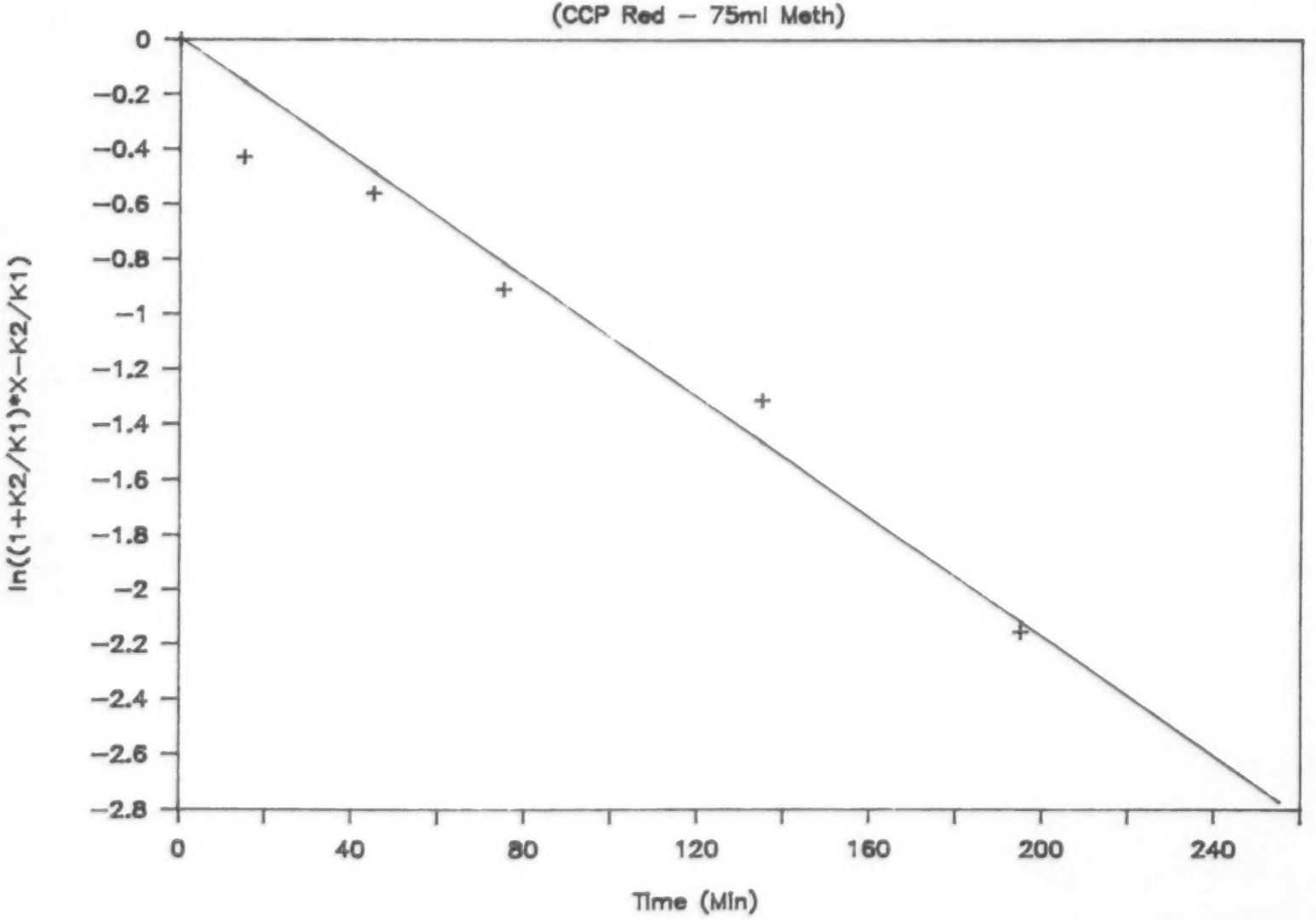


Figure 56 - *K1 vs % Suppressant*

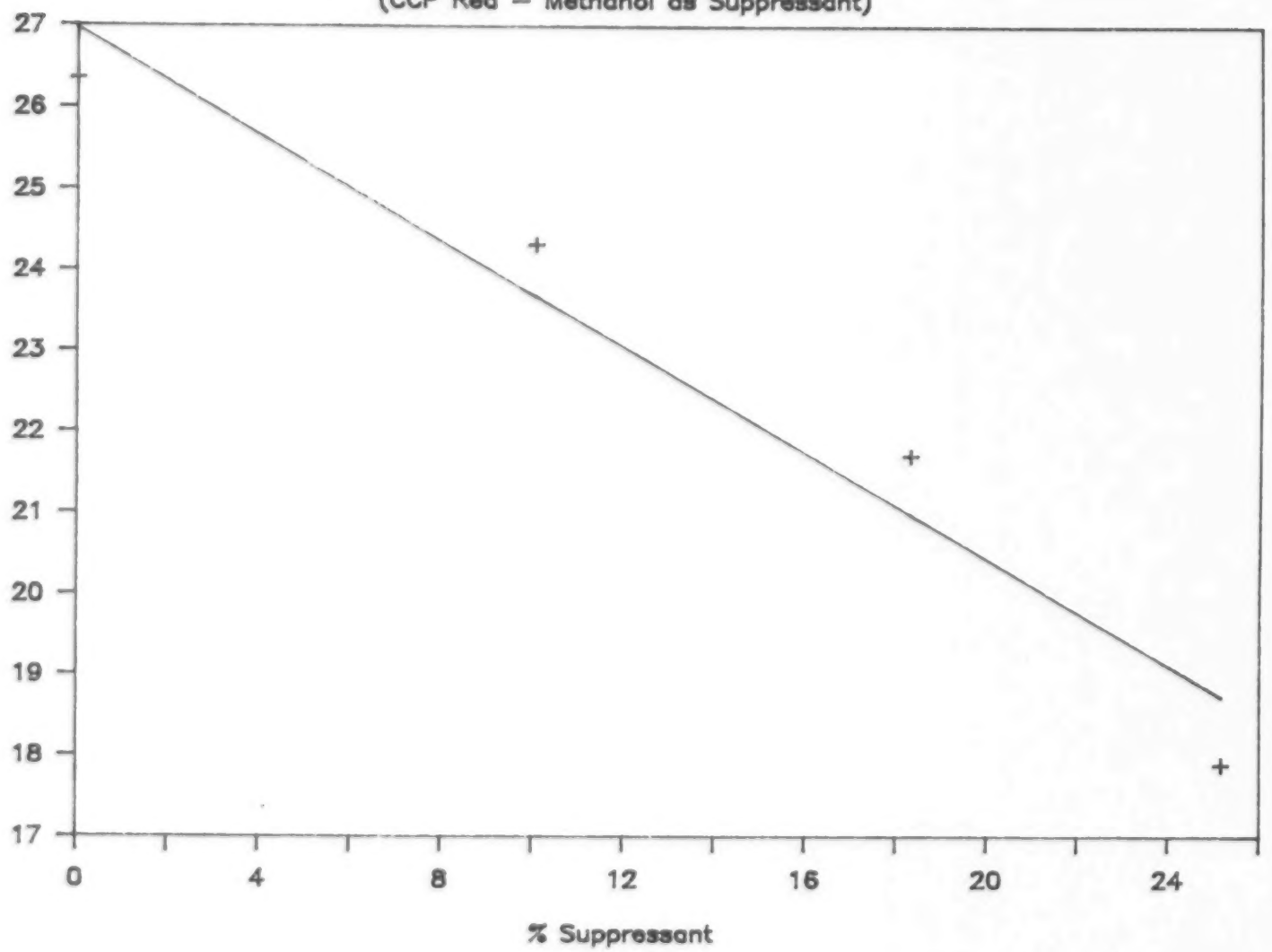
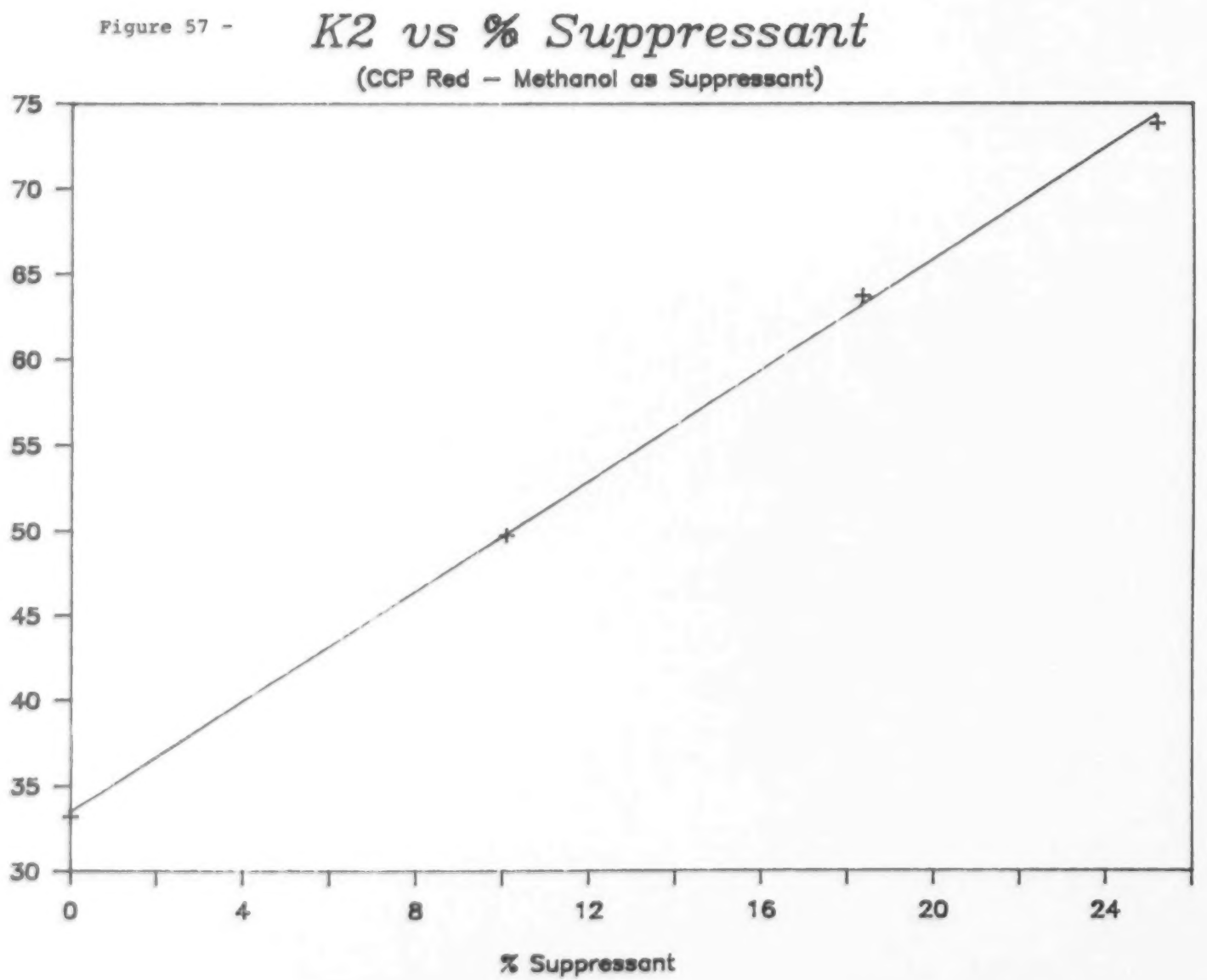


Figure 57 -


K2 vs % Suppressant
(CCP Red – Methanol as Suppressant)
75
70
65
60
55
50
45
40
35
30
K2
0
4
8
12
16
20
24
% Suppressant

Brine dissolved some particles, while passing the vertical core. The Concentration of ions in the brine versus time was recorded for each core sample in Tables 19 through 40 inclusive.

The reaction that takes place in this set of experiments can be classified as a heterogeneous reaction. A reaction is heterogeneous if it requires the presence of at least two phases to proceed at the rate that it does. It is immaterial whether the reaction takes place in one, two, or more phases, or at an interface[5]. The rate equation is more complicated, since more than one phase is present and the movement of the materials from one phase to another must be considered as well. Thus the rate expression in general should incorporate mass transfer terms in addition to the usual chemical kinetic term. The overall rate expression, therefore, should incorporate both physical transport and reaction steps. In fluid-solid noncatalytic reactions, the resistances to reaction can be considered to occur in series. The overall change requires that a number of steps take place in succession, then at steady state all these steps will proceed at the same rate. Thus,

$$r_{overall} = r_1 = r_2 = \ldots = r_m$$

For the reversible reaction:

$$A(liquid) + B(solid) \rightleftharpoons R(liquid) \qquad (20)$$

Dilute A diffuses through a stagnant film onto a plane surface consisting of B. There A and B react to yield liquid product (R) which diffuses back through the film into the main liquid stream. The flux of A to the surface Figure 58 is given by:

$$Q1 = \frac{1}{S}\frac{dN_A}{dt} = -D\frac{\Delta C}{\Delta x} = -\frac{D}{\Delta x}(C1 - C_s) = -K1(C1 - C_s) \qquad (21)$$

Table 19 - Concentration of the Ions in the Solution vs Time
(Core Sample A)

Time(Min)	Concentration of the ions in the solution(G/L)					
	SO4--	Cl-	Ca++	Mg++	K+	Na+
15.00	0.56	196.38	11.49	3.85	5.16	104.19
45.00	0.57	187.89	11.22	3.51	4.94	99.76
75.00	0.56	194.24	11.27	3.67	4.98	103.49
105.00	0.59	201.25	11.54	3.63	5.03	107.81
135.00	0.55	194.11	11.25	3.58	4.90	103.65
165.00	0.55	193.66	11.28	3.46	4.85	103.57
195.00	0.57	195.83	11.29	3.58	4.93	104.71
225.00	0.57	199.82	11.38	3.53	4.95	107.27
240.00	0.55	197.79	11.25	3.65	4.95	105.88
270.00	0.71	263.45	11.97	4.14	5.85	146.26
300.00	0.58	195.90	11.35	3.51	4.85	104.87
330.00	0.71	242.16	13.34	3.53	5.73	132.10
360.00	0.77	265.92	14.26	4.67	6.04	144.15
390.00	0.75	270.81	14.10	4.34	6.01	148.13
420.00	0.78	272.64	14.09	4.32	5.85	149.50
450.00	0.77	279.08	14.21	4.80	5.98	152.53
480.00	0.56	196.39	10.00	3.93	5.02	105.84

Table 20 - Concentration of the Ions in the Solution vs Time
(Core Sample E)

Time (Min)	CONCENTRATION OF THE IONS IN THE SOLUTION (G/L)						
	HCO3-	SO4--	Cl-	Ca++	Mg++	K+	Na+
4.00	0.03	2.73	188.86	11.26	3.50	4.94	101.41
15.00	0.03	1.98	193.72	12.14	3.58	5.08	102.94
30.00	0.04	1.88	194.84	11.96	3.71	5.02	103.63
45.00	0.03	1.80	194.67	11.81	3.58	4.91	103.98
60.00	0.03	1.58	194.41	11.50	3.56	4.83	104.14
75.00	0.04	1.81	192.93	11.65	3.55	4.89	103.08
90.00	0.03	1.67	194.14	11.78	3.38	4.98	103.91
105.00	0.04	1.78	193.66	11.64	3.86	4.89	102.97
120.00	0.04	1.39	194.79	11.47	3.50	4.87	104.41
135.00	0.04	1.48	194.81	11.44	3.30	4.85	104.88
152.00	0.04	1.63	193.02	11.70	3.59	4.88	102.94
165.00	0.04	1.35	196.67	11.48	3.48	4.85	105.63
180.00	0.04	1.73	194.77	11.64	3.42	4.95	104.47

Table 21 - Concentration of the Ions in the Solution vs Time
(Core Sample F)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	Cl-	Ca++	Mg++	K+	Na+
2.00	0.62	176.15	11.77	3.61	4.94	91.35
17.00	0.54	177.78	11.92	3.43	4.94	92.55
30.00	0.79	181.00	11.76	5.22	5.14	91.43
45.00	0.50	178.36	11.92	3.25	4.94	93.23
60.00	0.54	177.93	11.81	3.14	4.85	93.37
75.00	0.54	176.86	12.01	3.09	4.96	92.47

Table 22 - Concentration of the Ions in the Solution vs Time
(Core Sample G)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	CL-	Ca++	Mg++	K+	Na+
2.00	3.37	192.18	11.45	3.54	4.92	103.74
20.00	2.89	191.67	11.44	3.86	5.12	102.30
25.00	3.44	195.58	12.07	3.43	5.29	105.11
30.00	3.81	191.07	11.43	3.80	5.15	102.46
35.00	4.31	191.13	11.85	3.45	5.22	102.89
42.00	2.33	193.30	11.33	3.38	5.05	104.17
45.00	2.62	196.53	11.50	3.65	4.98	105.74
50.00	2.78	190.55	12.10	3.37	5.20	101.64
57.00	2.74	181.24	11.47	3.32	5.48	96.24
62.00	2.99	173.39	11.52	3.33	6.42	90.66

Table 23 - Concentration of the Ions in the Solution vs Time
(Core Sample H)

Time(Min)	Concentration of the ions in the solution(G/L)					
	SO4--	Cl-	Ca++	Mg++	K+	Na+
1.00	0.35	193.42	21.54	3.96	4.76	90.66
5.00	0.35	194.14	21.98	4.14	4.85	90.22
10.00	0.33	196.18	22.37	3.90	4.90	91.53
15.00	0.34	193.63	21.78	3.96	4.76	90.35
30.00	0.35	198.00	21.88	3.88	4.82	93.35
45.00	0.36	197.23	22.00	4.07	4.77	92.38
60.00	0.32	196.75	21.63	4.07	4.78	92.47
75.00	0.30	196.52	21.59	4.00	4.67	92.56
90.00	0.32	194.15	21.45	3.87	4.70	91.42
107.00	0.33	198.12	22.02	4.10	4.72	92.90
120.00	0.34	197.56	21.74	3.92	4.70	93.22
135.00	0.36	195.31	21.88	3.85	4.72	91.72
150.00	0.35	193.63	21.64	3.69	4.78	91.18
165.00	0.40	195.83	21.97	3.81	4.72	92.06
180.00	0.36	194.35	21.54	3.81	4.69	91.59
210.00	0.34	195.13	21.75	3.86	4.73	91.72
241.00	0.35	198.51	21.68	4.04	4.97	93.53
250.00	0.33	196.55	21.70	4.00	4.78	92.41
252.00	0.35	194.84	21.52	4.04	4.68	91.49
265.00	0.38	194.01	21.44	3.88	4.66	91.38
280.00	0.35	195.79	21.72	3.85	4.66	92.25
310.00	0.34	197.26	21.57	3.92	4.73	93.21
340.00	0.34	197.33	21.76	4.07	4.65	92.80
370.00	0.36	195.42	21.82	3.94	4.71	91.71

Table 24 - Concentration of the Ions in the Solution vs Time
(Core Sample I)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	Cl-	Ca++	Mg++	K+	Na+
5.00	0.50	171.90	9.10	3.40	4.80	92.00
15.00	0.47	170.90	9.10	3.20	4.70	91.80
30.00	0.50	171.10	9.20	3.40	4.80	91.50
49.00	0.50	169.90	9.10	2.90	4.70	92.00
60.00	0.50	175.90	9.20	3.40	4.80	94.60
76.00	0.45	173.50	9.20	3.20	4.70	93.40
90.00	0.54	177.50	9.40	3.60	4.80	95.10
105.00	0.68	174.50	9.50	3.40	4.80	93.30
120.00	0.49	175.00	9.60	3.20	5.00	93.70
135.00	0.52	176.00	9.20	3.40	4.70	94.70
150.00	0.47	175.50	9.30	3.20	4.70	94.60
165.00	0.49	176.90	9.40	3.20	4.80	95.40

Table 25 - Concentration of the Ions in the Solution vs Time
(Core Sample K)

Time(Min)	Concentration of the ions in the solution(G/L)					
	SO4--	CL-	CA++	MG++	K+	NA+
3.00	5.10	163.90	9.97	2.85	3.62	89.92
10.00	3.59	157.12	9.53	3.13	3.57	84.72
15.00	3.64	162.56	9.45	3.34	3.52	87.98
20.00	3.98	167.81	9.90	2.99	3.71	91.59
25.00	4.16	164.93	9.69	3.14	3.51	89.87
31.00	4.79	166.53	9.85	3.02	3.47	91.29

Table 26 - Concentration of the Ions in the Solution vs Time
(Core Sample L)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	Cl-	CA++	MG++	K+	NA+
3.00	0.66	231.70	34.55	4.38	3.42	100.71
15.00	0.61	232.38	34.56	4.23	3.43	101.41
30.00	0.60	230.15	34.71	4.49	3.37	99.32
45.00	0.59	231.90	34.68	4.23	3.41	100.95
63.00	0.63	230.56	34.59	4.27	3.45	100.10
75.00	0.57	224.09	35.13	4.08	3.41	95.65
90.00	0.59	229.80	34.80	4.27	3.51	99.30
105.00	0.61	232.73	34.42	4.27	3.39	101.73
120.00	0.58	230.95	34.56	4.23	3.45	100.43
135.00	0.58	232.46	34.69	4.33	3.41	101.10
155.00	0.57	229.19	34.73	4.23	3.68	98.97
165.00	0.62	237.06	33.92	4.11	3.49	105.36
183.00	0.66	236.65	34.75	4.20	3.62	103.91
211.00	0.59	231.66	34.58	4.34	3.68	100.54
240.00	0.60	234.27	34.33	4.42	3.53	102.46
270.00	0.64	234.70	35.06	4.48	3.63	101.75
300.00	0.70	231.39	34.18	3.99	3.59	101.01
330.00	0.59	234.88	34.46	4.28	3.69	102.89
360.00	0.60	225.60	35.72	4.37	3.82	95.15
390.00	0.53	226.18	35.08	4.32	3.74	96.37
420.00	0.54	230.83	34.85	4.11	3.74	100.06
437.00	0.53	231.05	34.47	3.85	3.68	101.17

Table 27 - Concentration of the Ions in the Solution vs Time
(Core Sample M)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	Cl-	Ca++	Mg++	K+	Na+
2.50	0.64	186.79	10.89	3.48	5.02	99.46
16.00	0.68	193.41	10.80	3.25	4.94	104.37
31.00	0.65	186.93	10.54	3.42	4.87	100.18
45.00	0.64	191.75	10.73	3.29	4.86	103.32
60.00	0.64	191.15	10.57	3.09	4.80	103.54
78.00	0.64	192.95	10.74	3.20	4.83	104.28
90.00	0.66	191.92	10.81	3.29	4.76	103.40
106.00	0.69	186.56	10.61	3.42	4.70	99.97
120.00	0.63	189.91	10.44	3.44	4.31	102.50
138.00	0.63	188.71	10.20	3.14	4.11	102.68
144.00	0.66	189.41	10.20	3.21	3.92	103.13
180.00	0.68	191.17	10.26	3.26	3.85	104.16

Tablw 28 - Concentration of the Ions in the Solution vs Time
(Core Sample N)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	Cl-	Ca++	Mg++	K+	Na+
1.00	0.75	184.90	10.25	3.32	3.75	100.08
15.00	0.71	181.30	10.23	3.33	3.78	97.71
30.00	0.73	177.40	10.16	3.21	3.79	95.50
45.00	0.74	183.14	10.20	3.65	3.76	98.36
60.00	0.70	183.31	10.25	3.09	3.72	99.47
75.00	0.72	186.98	10.31	3.22	3.79	101.51
90.00	0.77	190.52	10.39	3.17	3.79	103.83
105.00	0.70	189.29	10.39	3.48	3.70	102.48
120.00	0.75	187.96	10.39	3.38	3.72	101.81
135.00	0.67	172.31	9.87	3.03	3.53	93.00
150.00	0.75	189.96	10.45	3.39	3.73	103.01
165.00	0.76	190.12	10.39	3.44	3.75	103.08
180.00	0.73	187.03	10.32	3.31	3.73	101.40
240.00	0.78	192.54	10.52	2.90	3.75	105.53
270.00	0.82	188.14	10.33	3.53	3.68	101.77
300.00	0.71	189.27	10.31	3.23	3.71	103.01
330.00	0.74	187.20	10.25	3.28	3.74	101.65
360.00	0.75	191.45	10.41	3.18	3.76	104.40

Table 29 - Concentration of the Ions in the Solution vs Time
(Core Sample O)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	CL-	CA++	Mg++	K+	NA+
4.00	1.10	201.32	9.34	3.39	4.06	111.64
15.00	2.05	204.73	9.47	3.64	4.10	113.64
30.00	0.70	205.32	9.46	3.78	4.06	113.17
45.00	0.77	206.73	9.55	3.85	4.04	113.89
60.00	0.67	202.81	9.41	3.68	3.93	111.83
75.00	0.63	203.95	9.46	3.47	3.92	112.91
90.00	0.65	203.72	9.44	3.28	3.88	113.17
105.00	0.63	207.58	9.56	3.95	3.98	114.20
120.00	0.63	189.76	9.10	3.44	3.93	104.16
135.00	0.60	191.05	9.07	3.30	3.81	105.36
150.00	0.60	192.65	9.14	3.13	3.80	106.65
165.00	0.58	185.82	9.14	3.46	3.77	101.61
180.00	0.59	192.26	9.08	3.27	3.76	106.21
207.00	0.62	195.36	9.14	3.44	3.79	107.84
255.00	0.57	196.67	9.15	3.39	4.04	108.60
270.00	0.57	194.14	9.16	3.28	3.74	107.32
300.00	0.60	194.61	9.20	3.66	3.80	106.83
330.00	0.62	191.45	9.25	3.49	3.75	105.08
363.00	0.59	194.02	9.21	3.31	3.94	107.03
390.00	0.59	192.89	9.17	3.52	3.77	106.04
420.00	0.60	193.04	9.16	3.09	3.09	106.97
450.00	0.58	190.99	9.08	3.57	3.57	104.80

Table 30 - Concentration of the Ions in the Solution vs Time
(Core Sample P)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	Cl-	Ca++	Mg++	K+	Na+
6.00	0.53	161.39	10.49	2.88	3.59	85.38
15.00	0.59	163.10	10.57	2.97	3.72	86.17
32.00	0.57	160.95	10.54	3.36	3.61	84.12
45.00	0.56	161.11	10.43	3.17	3.59	84.73
60.00	0.55	161.28	10.36	2.92	3.58	85.39
75.00	0.54	161.35	10.41	3.27	3.58	84.70
90.00	0.53	158.39	10.39	2.91	3.51	83.53
105.00	0.54	157.21	10.29	2.88	3.52	82.94
120.00	0.56	161.07	10.33	3.20	3.55	84.79
135.00	0.55	160.80	10.32	3.12	3.54	84.77
150.00	0.54	160.15	10.37	3.28	3.60	83.95
165.00	0.51	159.88	10.46	3.22	3.67	93.73

Table 31 - Concentration of the Ions in the Solution vs Time
(Core Sample Q)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	CL-	Ca++	Mg++	K+	Na+
4.00	0.66	206.15	24.23	3.86	3.62	96.85
15.00	0.73	216.86	23.28	4.05	3.62	104.55
30.00	0.71	208.46	23.90	3.83	3.50	98.87
45.00	0.76	214.05	23.56	3.60	3.53	103.34
60.00	0.70	205.35	24.34	3.77	3.63	96.40
75.00	0.61	213.22	24.36	3.90	3.63	101.18
90.00	0.60	207.22	24.35	3.88	3.66	97.33
105.00	0.59	213.13	24.36	4.06	3.74	100.74
120.00	0.62	218.00	24.47	3.77	3.70	104.36
138.00	0.74	213.08	24.79	3.82	3.75	100.75
150.00	0.67	209.87	24.46	4.03	3.65	98.65
165.00	0.76	218.79	24.09	3.57	3.67	105.76
180.00	0.66	215.20	23.99	4.00	3.65	102.72
214.00	0.68	220.95	25.12	4.13	3.71	104.89
240.00	0.65	211.89	25.10	4.13	3.91	98.91
270.00	0.71	219.13	23.76	4.05	3.69	105.42
300.00	0.64	218.05	24.33	4.06	3.64	104.04
330.00	0.67	219.23	24.58	3.89	3.66	104.86
360.00	0.60	216.20	24.12	4.07	3.65	103.05
400.00	0.64	220.98	24.69	4.04	3.65	105.58
420.00	0.69	217.72	24.54	3.92	3.74	103.81
444.00	0.61	210.85	24.72	3.92	3.69	99.16

Table 32 - Concentration of the Ions in the Solution vs Time
(Core Sample S)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	Cl-	CA++	Mg++	K+	Na+
3.00	2.90	176.59	10.84	2.92	4.23	95.51
15.00	3.02	175.87	10.83	3.25	4.14	94.55
30.00	2.74	169.94	10.47	3.04	4.02	91.44
45.00	2.17	173.94	10.25	3.14	3.93	93.90
60.00	2.47	175.12	10.39	3.03	3.92	94.86
75.00	2.38	178.55	10.36	3.14	3.96	96.83
94.00	3.25	178.55	10.52	3.06	4.00	97.19
105.00	3.48	178.98	10.46	3.13	3.93	97.55
120.00	2.94	176.63	10.39	3.04	3.85	96.07
135.00	3.12	176.93	10.53	3.48	3.89	95.33

Table 33 - Concentration of the Ions in the Solution vs Time
(Core Sample T)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	Cl-	Ca++	Mg++	K+	Na+
3.50	0.81	199.84	10.96	3.51	22.28	97.73
15.00	0.81	202.99	10.80	3.38	22.28	100.20
30.00	0.77	195.59	10.97	3.30	22.78	95.04
45.00	0.60	199.36	11.05	3.29	23.04	97.18
60.00	0.66	206.10	10.83	3.51	22.58	101.69
76.50	0.68	201.38	10.93	3.67	22.88	98.05
90.00	0.63	200.61	11.03	3.44	23.11	97.71
106.00	0.61	200.85	10.95	3.43	22.98	98.04
120.00	0.64	204.71	10.96	3.76	23.00	99.91
135.00	0.65	208.15	10.91	3.75	22.90	102.29
150.00	0.60	199.45	11.11	3.40	23.23	96.84
165.00	0.56	194.77	10.47	3.76	22.31	94.38

Table 34 - Concentration of the Ions in the Solution vs Time
(Core Sample U)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	Cl-	Ca++	Mg++	K+	Na+
2.00	0.55	182.00	11.62	3.42	6.07	94.97
15.00	0.55	178.08	11.40	3.06	5.98	93.41
30.00	0.57	178.64	11.45	3.28	6.05	93.27
46.00	0.55	177.95	11.49	3.37	6.10	92.58
60.00	0.57	179.53	11.38	3.63	6.10	93.25
75.00	0.52	180.00	11.44	3.06	6.03	94.58
90.00	0.51	176.67	11.33	3.73	5.91	91.33
105.00	0.54	179.08	11.36	3.31	5.95	93.64
121.00	0.54	181.61	11.45	3.53	6.28	94.59
135.00	0.52	176.27	11.35	3.24	6.01	91.92
180.00	0.52	181.10	11.36	3.12	5.91	95.33

Table 35 - Concentration of the Ions in the Solution vs Time
(Core Sample V)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	CL-	Ca++	Mg++	K+	Na+
5.00	0.54	190.43	10.96	3.54	16.82	94.66
15.00	0.57	194.69	10.94	3.25	18.60	96.95
31.00	0.72	195.29	10.94	3.55	18.77	96.74
46.00	0.58	192.80	10.99	3.45	17.62	95.88
60.00	0.60	196.48	11.01	3.26	17.60	98.61
75.00	0.57	196.40	10.98	3.38	17.08	98.67
90.00	0.57	196.50	11.00	3.59	17.10	98.29
105.00	0.56	197.90	10.96	3.62	16.56	99.51
120.00	0.58	197.82	10.96	3.59	16.55	99.53
135.00	0.58	196.92	10.93	3.34	16.54	99.46
153.00	0.54	197.33	10.92	3.37	16.16	99.89
166.00	0.56	200.94	10.92	3.58	16.35	101.73
240.00	0.58	201.86	10.94	3.88	16.53	101.63

Table 36 - Concentration of the Ions in the Solution vs Time
(Core Sample W)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	CL-	Ca++	Mg++	K+	Na+
6.00	0.53	154.57	8.38	3.42	4.93	81.56
15.00	0.51	158.20	8.44	3.16	4.89	84.35
30.00	0.53	158.26	8.47	3.15	4.91	84.37
45.00	0.51	160.69	8.49	3.01	4.93	86.17
60.00	0.54	158.34	8.47	3.09	4.97	84.50
75.00	0.51	159.99	8.53	3.07	4.95	85.55
90.00	0.52	161.92	8.51	3.06	4.96	86.82
105.00	0.48	157.51	8.51	3.30	4.89	83.54
120.00	0.48	149.01	8.11	2.87	4.74	79.40
135.00	0.52	159.51	8.51	3.17	4.96	85.06
151.00	0.51	160.55	8.58	3.06	4.94	85.87
170.00	0.52	162.20	8.53	2.90	5.03	87.27
180.00	0.49	162.28	8.60	2.98	4.95	87.11
210.00	0.50	163.28	8.63	3.27	4.97	87.16
270.00	0.51	161.50	8.71	3.11	5.05	86.20

Table 37 - Concentration of the Ions in the Solution vs Time
(Core Sample WX)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	Cl-	Ca++	Mg++	K+	Na+
3.00	0.48	183.15	8.71	3.19	52.23	72.31
15.00	0.47	189.56	8.44	3.07	48.51	79.18
30.00	0.49	194.66	8.46	3.16	51.05	80.81
45.00	0.51	226.74	7.54	3.22	46.58	105.21
60.00	0.50	195.36	8.42	3.00	51.08	81.61
75.00	0.54	197.91	8.44	3.20	50.87	83.01
90.00	0.53	202.33	8.53	3.45	51.36	85.00
106.00	0.48	198.37	8.37	3.25	51.37	82.96
120.00	0.45	196.27	8.42	3.40	50.82	81.57
135.00	0.50	201.45	8.57	3.30	51.91	84.33
150.00	0.52	195.52	8.62	3.43	52.04	80.12

Table 38 - Concentration of the Ions in the Solution vs Time
(Core Sample WY)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	CL-	CA++	Mg++	K+	Na+
4.00	0.55	227.16	34.51	4.24	4.76	97.24
15.00	0.54	229.86	34.69	4.19	4.76	98.86
30.00	0.57	231.73	34.63	4.44	4.77	99.68
45.00	0.53	228.91	34.51	4.11	4.79	98.59
60.00	0.52	228.73	34.64	4.18	4.79	98.18
78.00	0.54	234.97	34.80	4.33	4.76	101.79
90.00	0.54	233.06	34.73	3.88	4.78	101.47
105.00	0.54	234.33	34.86	4.01	4.79	101.89
120.00	0.55	235.89	34.86	4.39	4.80	102.18
137.00	0.57	232.75	34.55	4.42	4.79	100.47
150.00	0.54	234.28	34.72	4.40	4.78	101.30
165.00	0.57	233.79	34.85	4.01	4.81	101.55
180.00	0.57	231.65	34.83	4.39	4.74	99.52
225.00	0.57	233.93	35.10	4.15	4.76	101.13
240.00	0.60	236.92	34.28	4.49	4.79	103.37
270.00	0.58	236.20	35.42	3.98	4.77	102.55
300.00	0.57	233.95	35.00	4.37	4.86	100.79
330.00	0.56	239.61	35.14	3.93	4.87	105.11
360.00	0.55	238.16	35.34	4.56	4.81	102.78
390.00	0.58	237.59	35.03	4.51	4.86	102.86
420.00	0.61	241.58	35.37	4.38	4.91	105.28

Table 39 - Concentration of the Ions in the Solution vs Time
(Core Sample Y)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	CL-	CA++	MG++	K+	NA+
5.00	0.55	195.56	10.77	3.70	5.22	104.72
15.00	0.57	194.10	10.75	3.43	5.17	104.35
30.00	0.58	195.55	10.79	3.41	5.13	105.30
45.00	0.53	195.50	10.77	3.78	5.20	104.53
60.00	0.56	195.24	10.85	3.54	5.19	104.74
75.00	0.54	196.08	10.92	3.56	5.21	105.17
90.00	0.66	194.99	10.89	3.85	5.16	103.97
105.00	0.56	199.00	9.41	3.80	5.23	108.32
120.00	0.59	200.57	9.41	3.58	5.22	109.79
135.00	0.56	200.07	9.43	3.46	5.23	109.64
153.00	0.58	206.55	9.58	3.87	5.25	112.89
165.00	0.56	205.02	9.55	3.48	5.30	112.64
180.00	0.57	204.97	9.58	3.73	5.28	112.12
210.00	0.59	208.07	9.60	3.46	5.27	114.62
240.00	0.59	205.36	9.52	3.54	5.23	112.84
270.00	0.59	207.85	9.74	3.93	5.94	113.05
300.00	0.56	204.90	9.61	3.86	5.78	111.49
331.00	0.58	206.41	9.68	3.53	5.94	112.94
368.00	0.60	204.33	9.65	3.65	5.95	111.40

Table 40 - Concentration of the Ions in the Solution vs Time
(Core Sample Z)

Time(Min)	Concentration of the ions in the solution (G/L)					
	SO4--	Cl-	Ca++	Mg++	K+	Na+
5.00	0.51	181.64	8.66	3.51	51.43	71.26
15.00	0.49	180.52	8.61	3.37	50.64	71.31
30.00	0.50	182.08	8.60	3.31	51.70	71.83
45.00	0.49	182.99	8.54	3.40	51.80	72.26
60.00	0.51	178.80	8.67	3.62	50.97	69.47
76.00	0.50	185.07	8.58	3.26	51.68	73.90
91.00	0.49	185.66	8.63	3.21	51.73	74.29
105.00	0.49	185.23	8.59	3.24	52.05	73.82
120.00	0.50	186.52	8.53	3.29	51.79	74.79
135.00	0.49	184.45	8.64	3.35	51.83	73.17
150.00	0.51	186.71	8.80	3.16	51.56	74.98
165.00	0.47	186.38	8.61	3.14	50.91	75.40
175.00	0.50	186.95	8.64	3.23	51.32	75.32

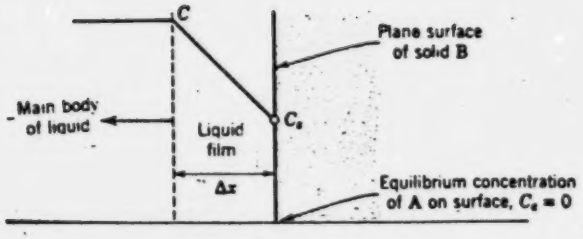


Figure 58

If the reaction is first order, irreversible with respect to A, and based on a unit surface, we obtain

$$Qs = \frac{1}{S} \quad \frac{dN_A}{dt} = -K_s C_S \tag{22}$$

where k_S is the reaction rate constant and C_S is the concentration of A on the surface which cannot be measured. At steady state, the flow rate to the surface is equal to the reaction rate at the surface and therefore,

$$Ql = Q_s \tag{23}$$

From Equations 1 and 2

$$-Kl(C_1 - C_S) = -k_S C_S \tag{24}$$

Therefore

$$C_S = \frac{kl}{kl + k_S} Cl \tag{24a}$$

Replacing equation 24a in Equation 22

$$Q_S = \frac{1}{S} \quad \frac{dN_A}{dt} = \frac{1}{1/kl + 1/k_S} \quad Cl = -k_{overall} Cl \tag{25}$$

This result shows that 1/kl and $1/k_S$ are additive resistances. The addition of resistances is permissible only when the rate is a linear function of concentration and the processes occur in series such as the above example.

When the individual rate expressions are not linear then to bypass a cumbersome expression, we can use the concept of rate-controlling step. In such a case, we need to find out the major resistances to the overall change and the slowest step is the rate - controlling step.

In our CSTR test, we tried the highest rate of mixing and therefore, diffusion of reactants to the surface was a very fast process. Diffusion of the products from the surface to the main body of liquid was also a fast process (because of good mixing). Therefore, the slowest process was the reaction step which is considered as the rate-controlling step. Then the overall rate is given by:

$$Ql = Q_S = -k_1 C_A + K_2 C_R \tag{26}$$

for the first order, reversible reaction (verified in static test)

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} R \tag{27}$$

C_R can be written as

$$C_R = C_{Ao} - C_A \tag{28}$$

Replacing C_R in Equation 7, we obtain

$$Ql = Q_S = -k_1 C_A + k_2 C_{Ao} - K_2 C_A$$

$$Ql = Q_S = -(K_1 + K_2) C_A + K_2 C_{Ao} \tag{29}$$

After the reaction the brine becomes supersaturated with respect to several ions. In the following section, the affect of these suppressants on the solubility of core particles in brine will be discussed.

Brine Alone

Three different core samples of O, A and Y were treated with brine alone.

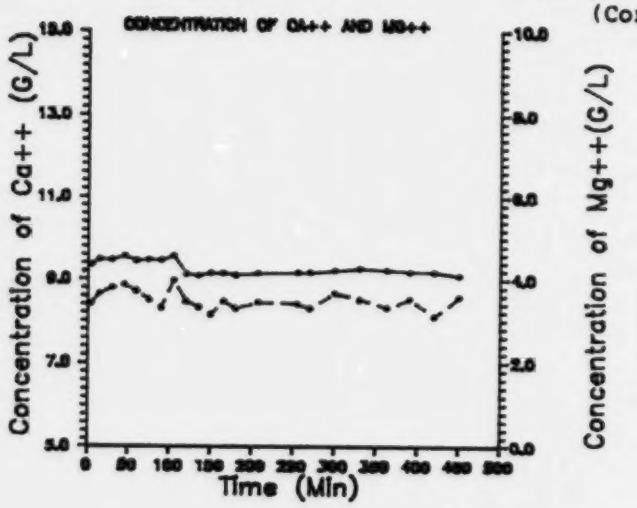
Brine dissolves KCL and NaCl particles from the cores in O and Y-series. The drop in Na^+ and Cl^- ion in O-series shows the precipitation of NaCl from the solution (Figure 59). The other ions remain almost unchanged. The increase in concentration of Cl^-, Na^+ and K^+ ions in Y-series (Figure 60) shows the dissolution of NaCl first and KCl later in the process. In A-series (Figure 61), dissolution and precipitation of all kinds of compounds in the brine after 200 minutes takes place. Before this time, only NaCl was dissolving in the brine. Brine dissolves ions from the core and leaves small crevices. Some of these crevices were later filled with precipitate. Figure 62 shows the core after 8 hours of treatment with brine.

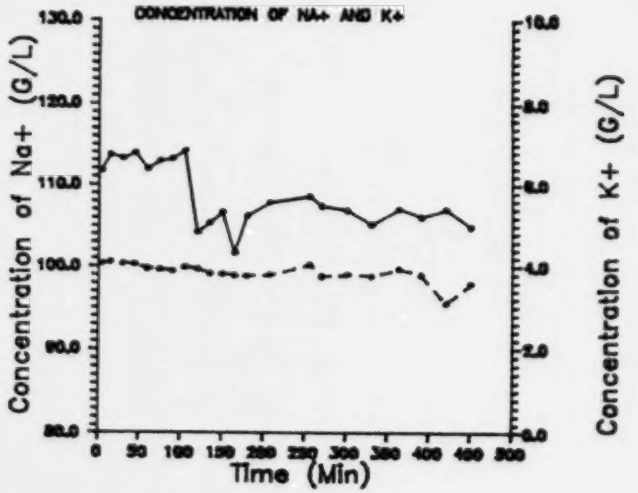
Brine + $CaCl_2$ as Suppressants

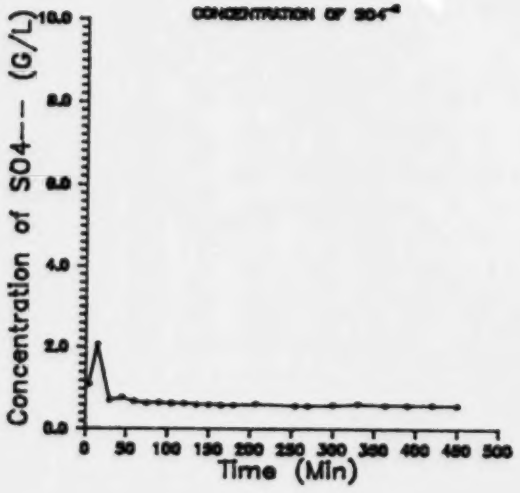
$CaCl_2$ was added to the brine as a suppressant. This addition caused the precipitation of NaCl in the solution. In the analyses of the solution, mixtures of the solution and the precipitate were used. The peaks, therefore, signify the dissolution of particles from the core. Mixtures of brine and $CaCl_2$ forms a slurry and does not cause plugging of the fluid in the vessel. Four core samples of L, Q, H and WY were used in these experiments. H and Q were treated with brine + 33.3 g/L $CaCl_2$. L and WY were treated with brine + 66.6 g/L $CaCl_2$.

This solution left very small holes in H and WY cores. Figures 63 and 64 indicate that only very small changes in concentration of Cl^-, Ca^{++} and Mg^{++} has taken place. Changes in Na^+ and K^+ are also very small. Holes created in cores Q and L are significant and they were not filled with any precipitate because the particles are in colloidal form in the solution. There were significant changes in concentration of Na^+, Ca^{++} and Cl^- in both Q and L series. k^+ and Mg^{++} concentration remains almost constant (Figures 65 and 66). The increase in the amount of $CaCl_2$ from 33.3 g/L to 66.6 g/L does not seem to have a significant affect on solubility. There was no plugging problem in this set of experiments.

Figure 59 - Concentration of Different Ions in the Solution vs Time
(Core Sample O)







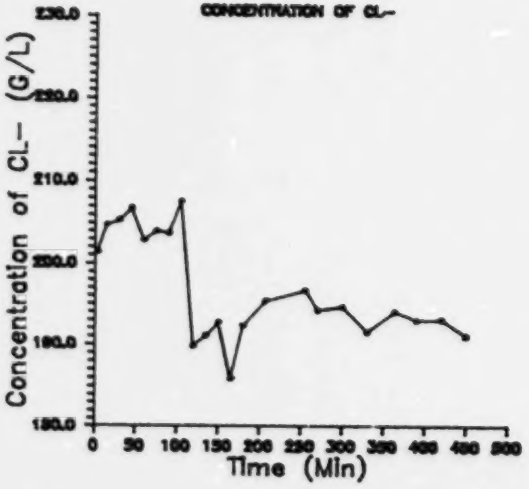
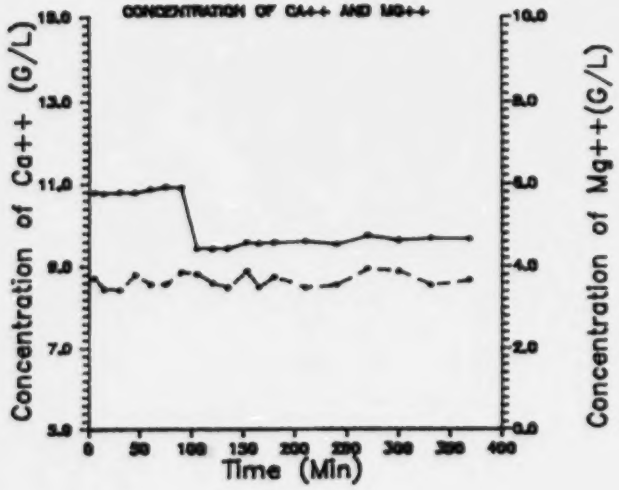
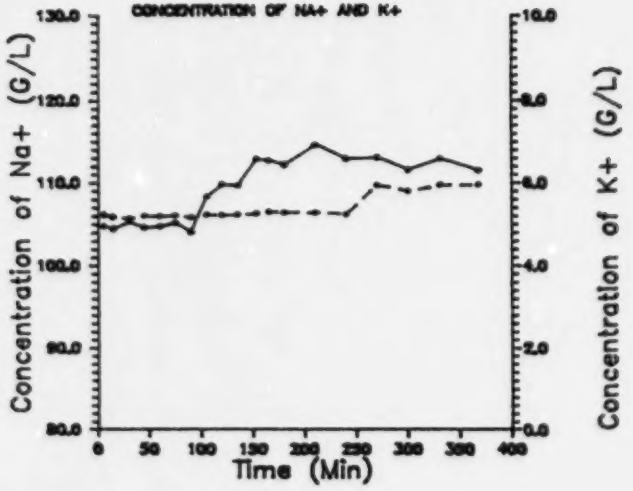
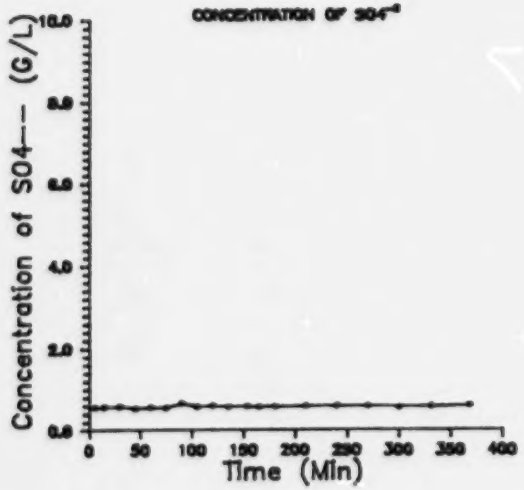


Figure 60 - Concentration of Different Ions in the Solution vs Time
(Core Sample Y)







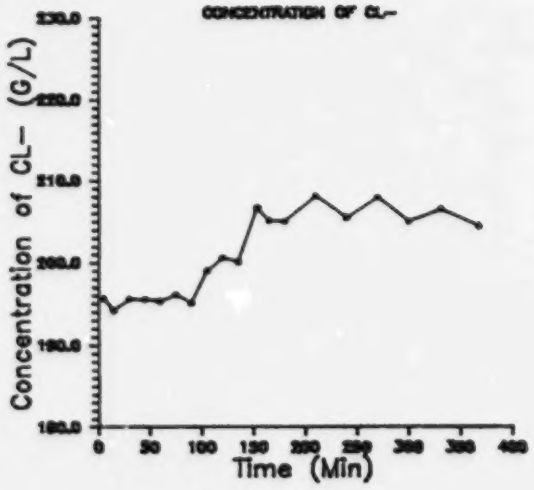
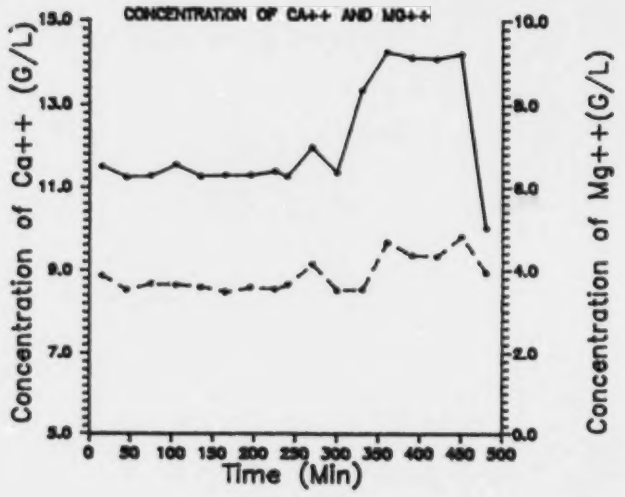
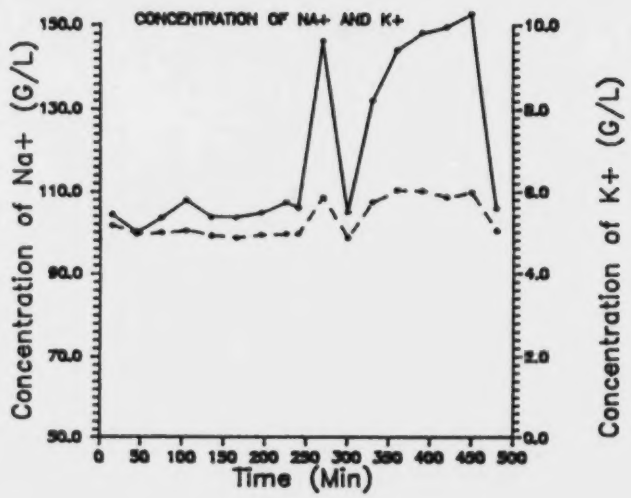
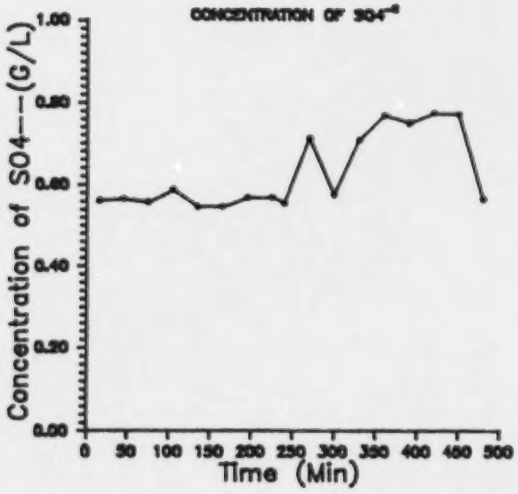
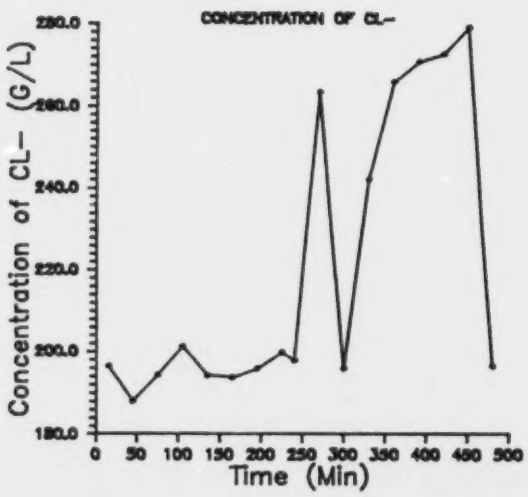


Figure 61 - Concentration of Different Ions in the Solution vs Time
(Core Sample A)









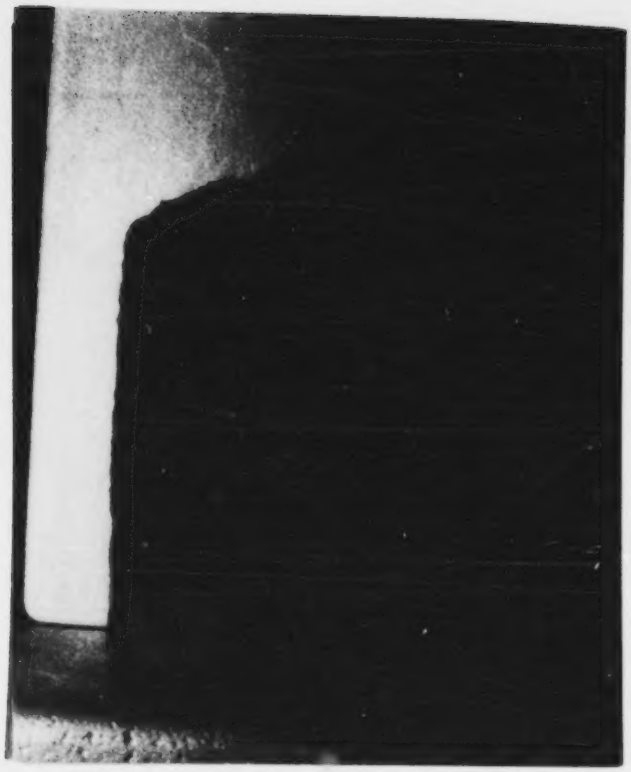
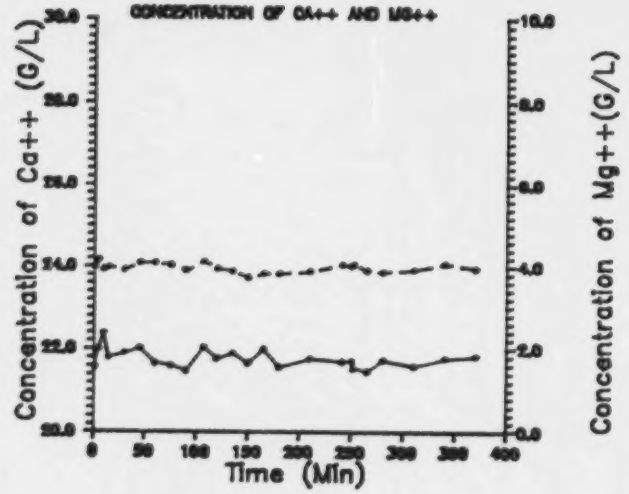
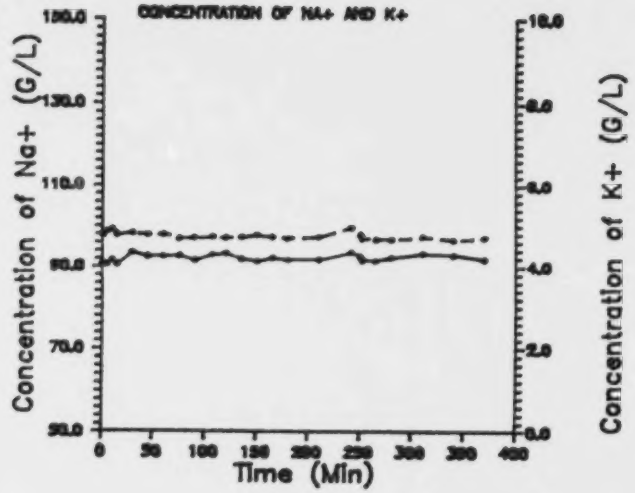
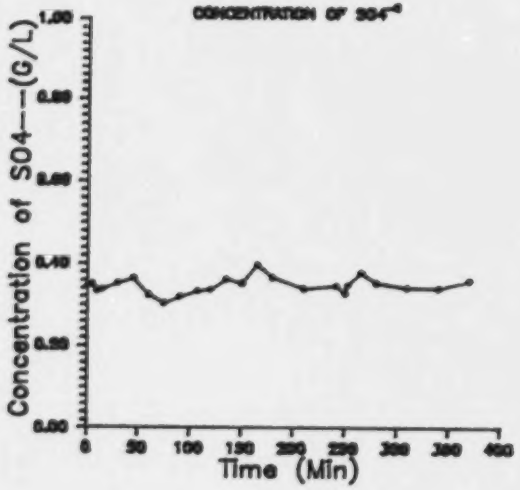


Figure 62 - Core Sample O - After the Experiment

Figure 63 - Concentration of Different Ions in the Solution vs Time
(Core Sample H)







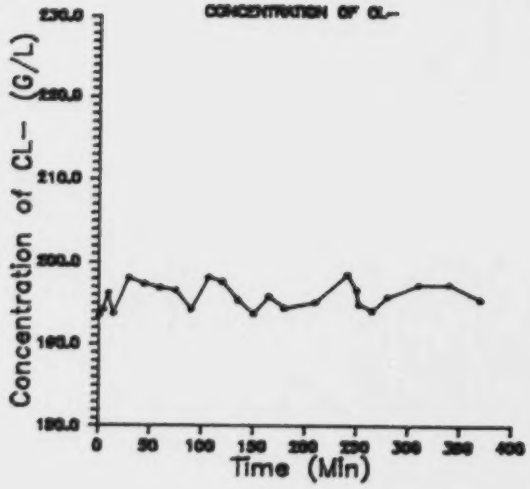
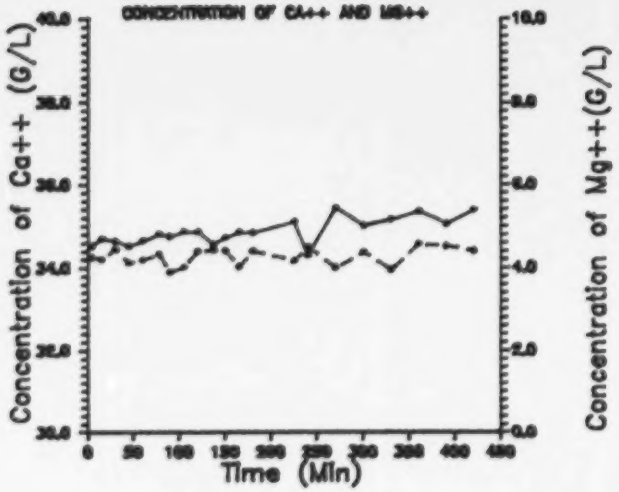
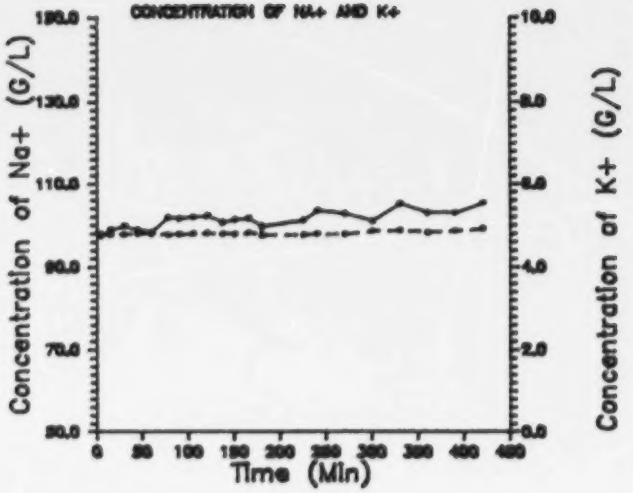
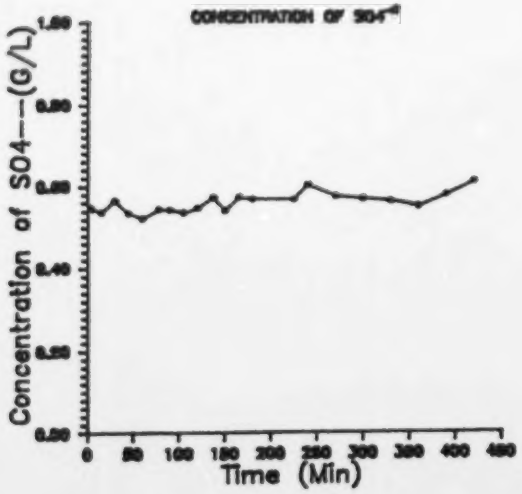


Figure 64 - Concentration of Different Ions in the Solution vs Time
(Core Sample WY)







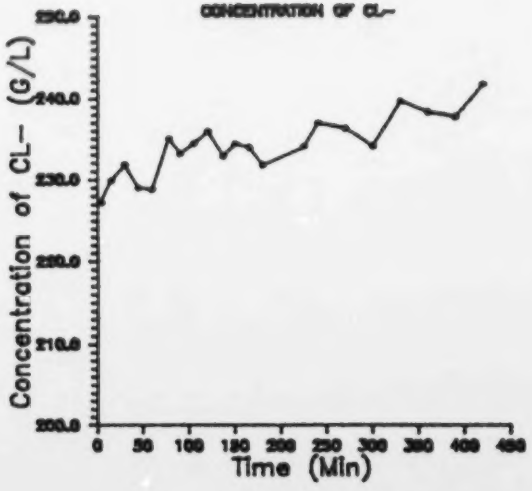
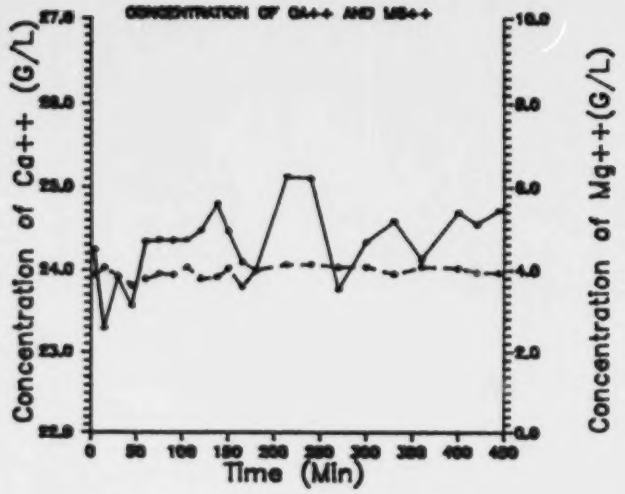
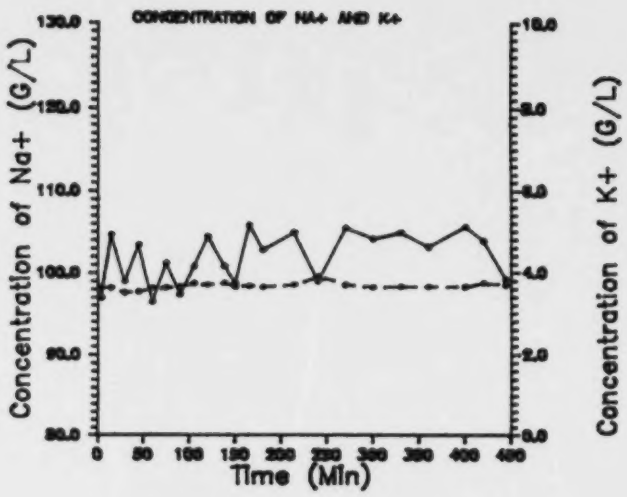
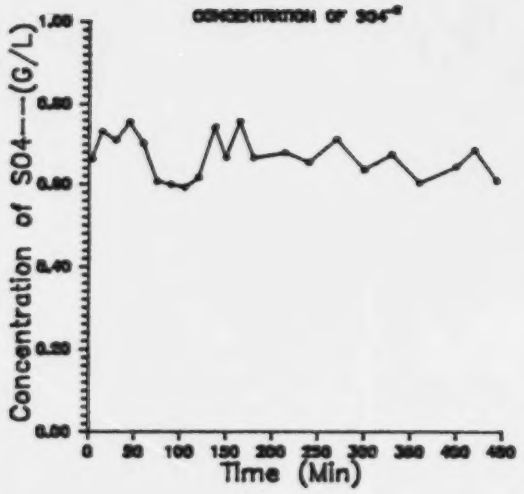


Figure 65 - Concentration of Different Ions in the Solution vs Time
(Core Sample Q)







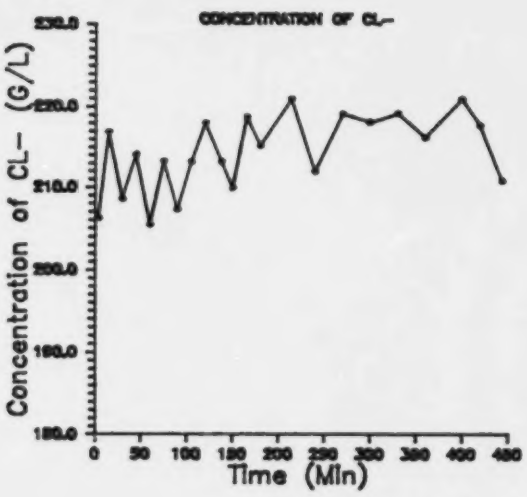
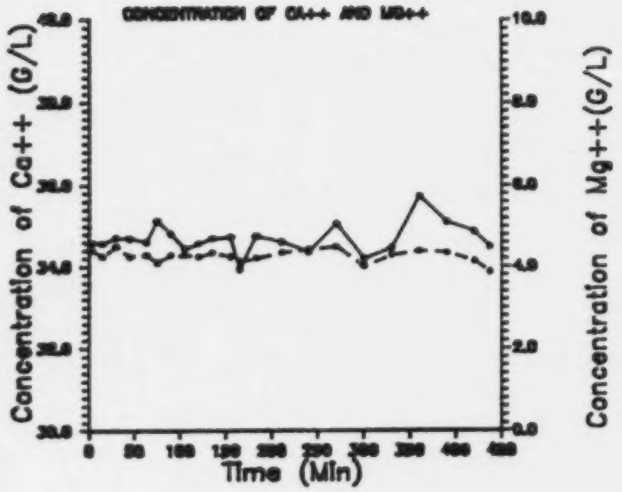
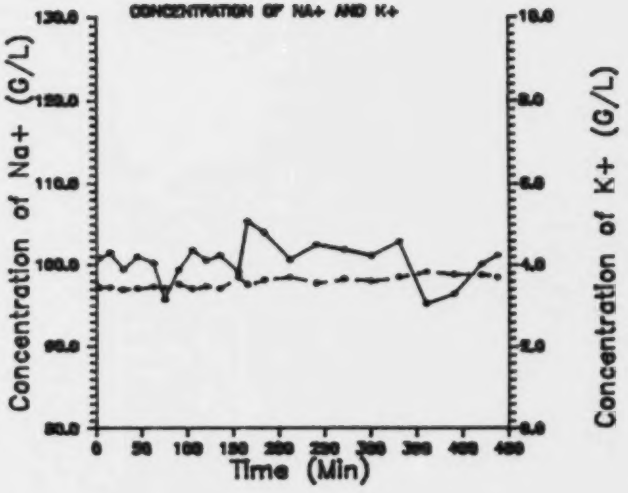
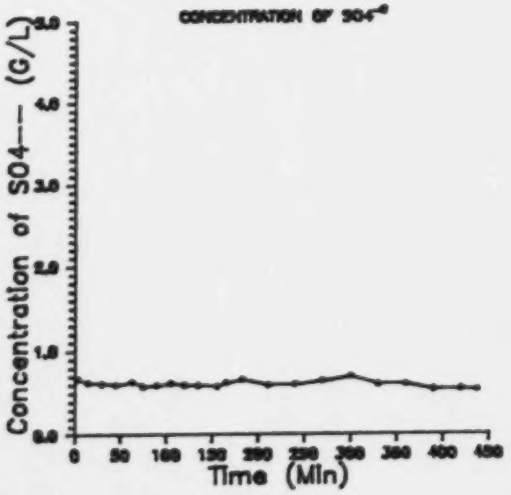
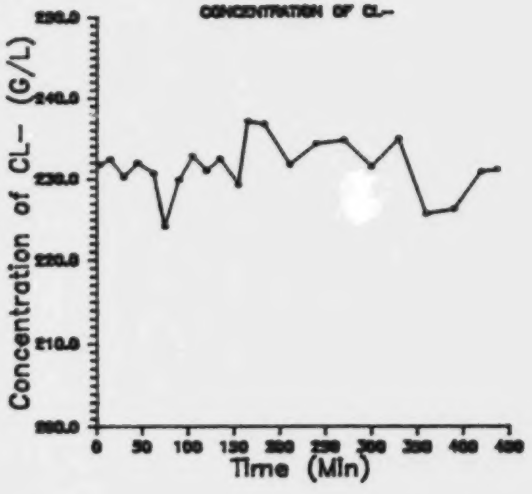


Figure 66 - Concentration of Different Ions in the Solution vs Time
(Core Sample L)









Figures 67 and 68 show pictures of two cores of H and Q after treatment.

Brine + Methanol as Suppressant

Different amounts of Methanol were added to the brine but the precipitate formed gradually filled up the vessel and plugged up the flow of fluid (Figure 69). In experiment with P cores, 70 mL of Methanol and 100 mL glycerol were added. Glycerol was added in order to increase the viscosity of the fluid. It was not very effective in reducing plugging. Experiments could not run for more than 2 to 3 hours because of plugging problems. Two core samples of P and V were left with big holes that were partially filled with precipitate. The other two samples had very small holes. Cores I, V and F were treated with brine and 70, 50 and 80 mL of Methanol per litre respectively.

Figures 70 and 71 show the concentration of ions with respect to time for cores F and I. Changes were observed in concentrations of Mg^{++}, K^{+} and Cl^{-}, indicating the dissolution of carnalite for F core (Figure 70). Changes in Na^{+}, Mg^{+} and Cl^{-}were observed for I core. Changes are gradual and not as significant as the changes with the brine or brine + $CaCl_2$. V core shows an increase in Cl^{-}, K^{+} and Na^{+}, showing the dissolution of potash and salt from the core (Figure 72). Concentration changes in the ions are insignificant for the P core (Figure 73), although, a large hole was observed in the core. This is due to the fact that precipitates were not included in the analyses of the solution. The results, therefore, don't specify the total concentration of the ions in the experiment. Pictures of cores of F and P are shown in Figures 74 and 75.

Brine + KCl

KCl was added to the brine before letting it pass the core. KCl addition causes saturation of the brine with respect to KCl and retards any further reaction between the brine and potash particles in the core. Addition of KCl causes the precipitation of NaCl. This precipitate gradually fills up the vessel

Figure 67 - Core Sample H - After Experiment

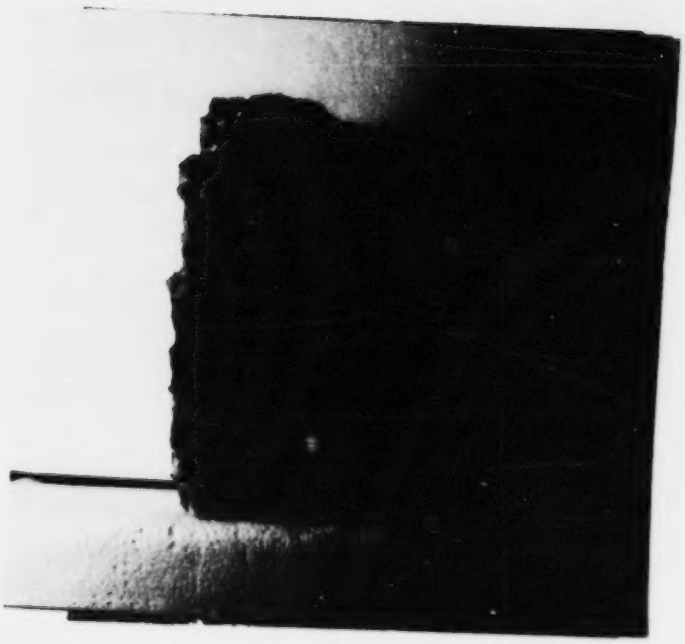


Figure 68 - Core Sample Q - After Experiment

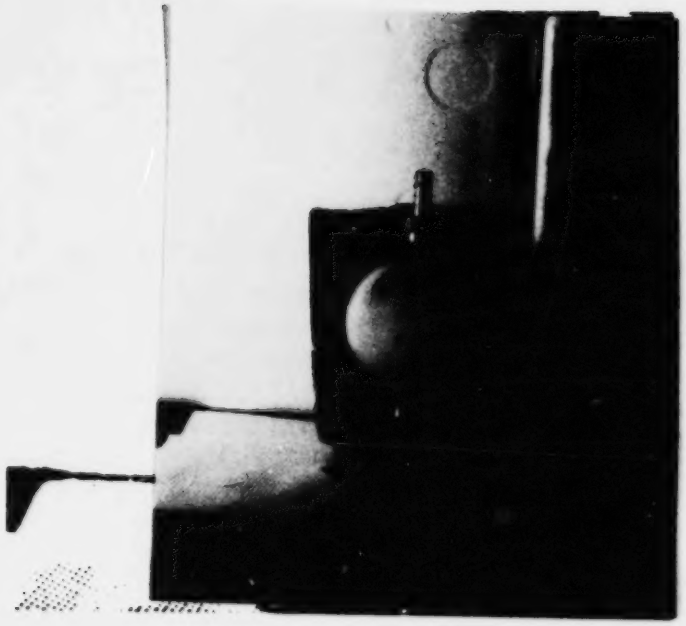
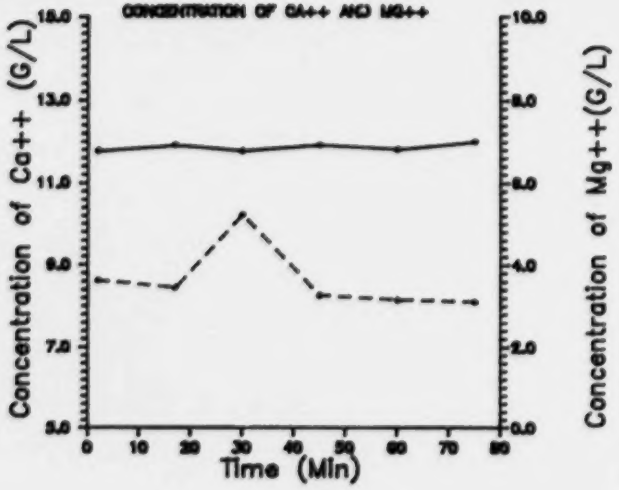
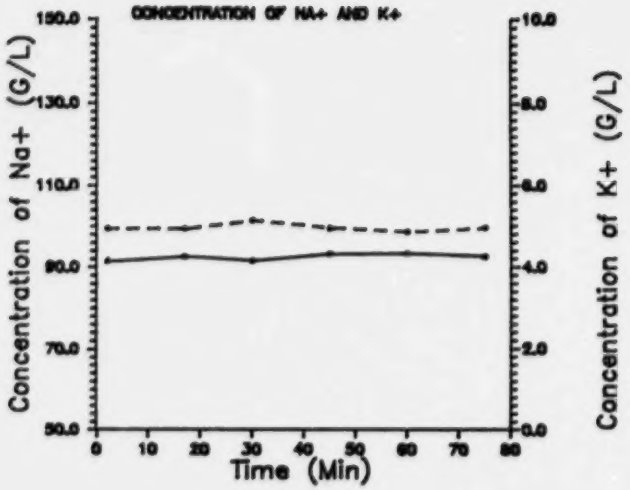
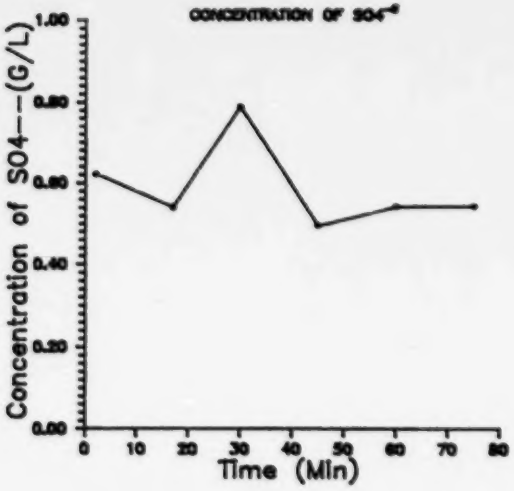


Figure 69 - Picture of the Vessel (After Plugging)

Figure 70 - Concentration of Different Ions in the Solution vs Time
(Core Sample F)







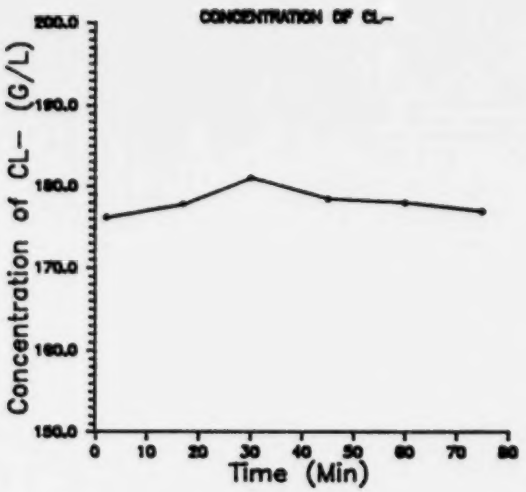
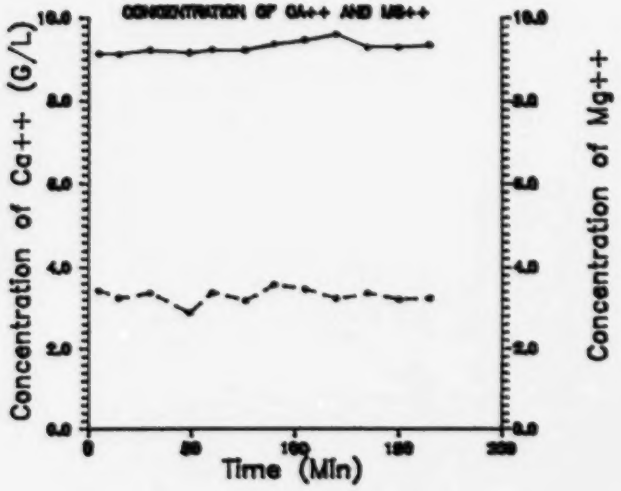
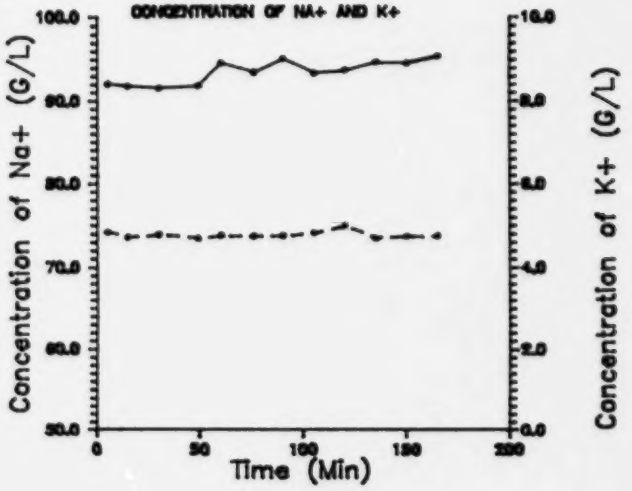
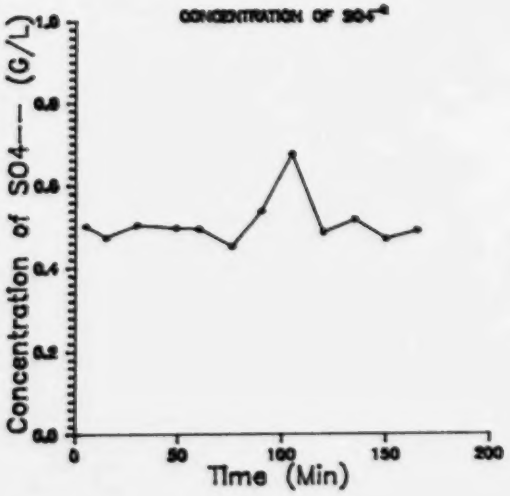


Figure 71 - Concentration of Different Ions in the Solution vs Time
(Core Sample I)







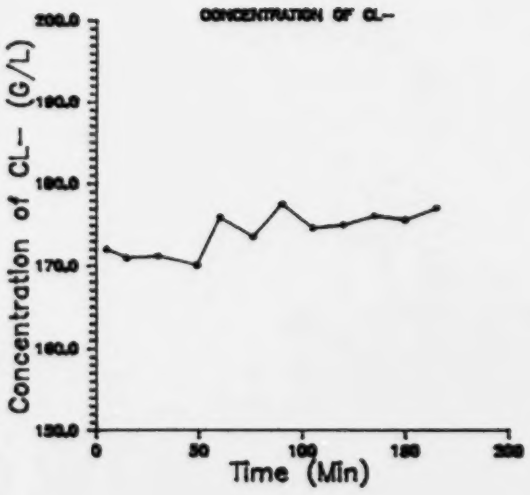
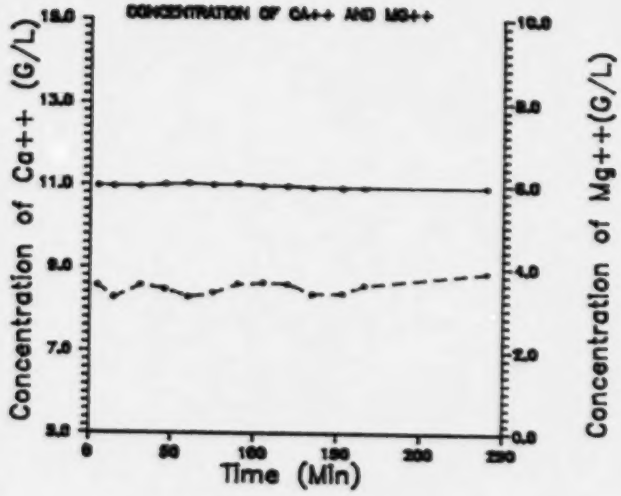
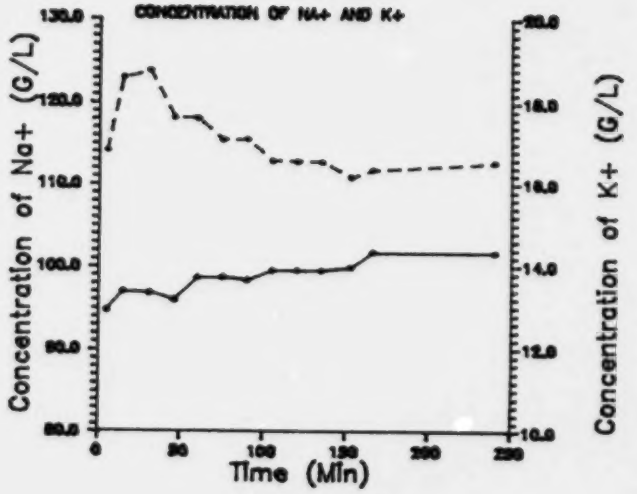
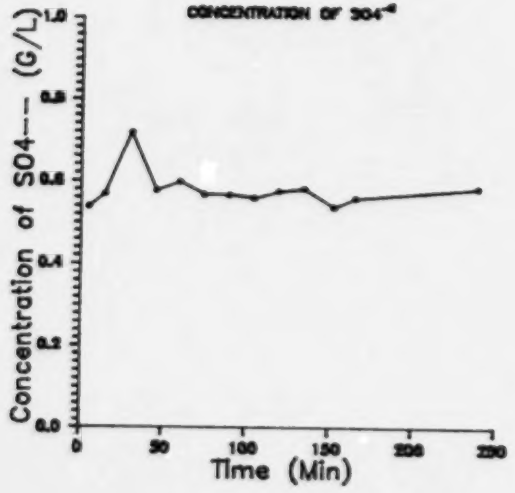


Figure 72 - Concentration of Different Ions in the Solution vs Time
(Core Sample V)







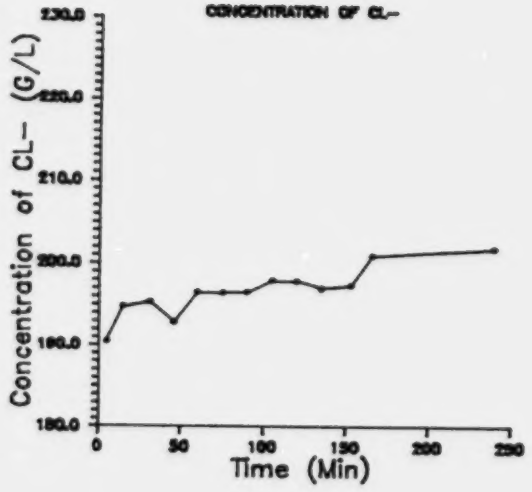
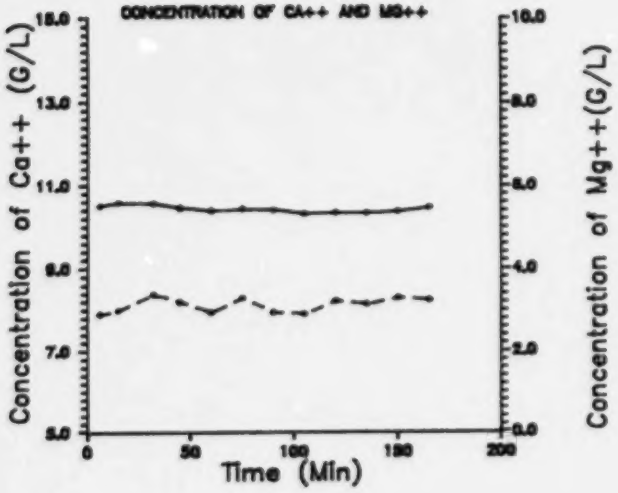
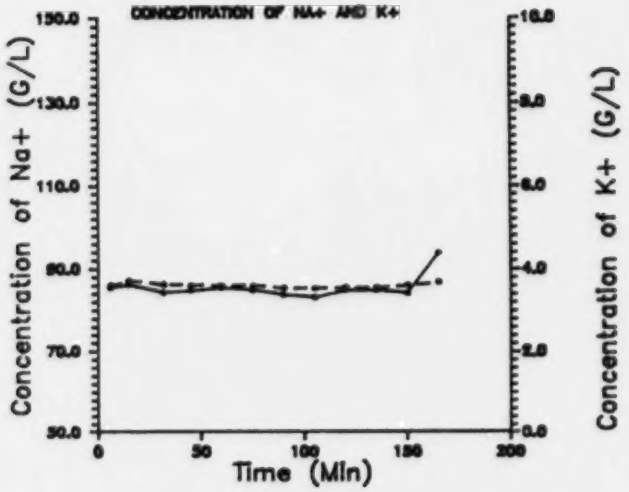
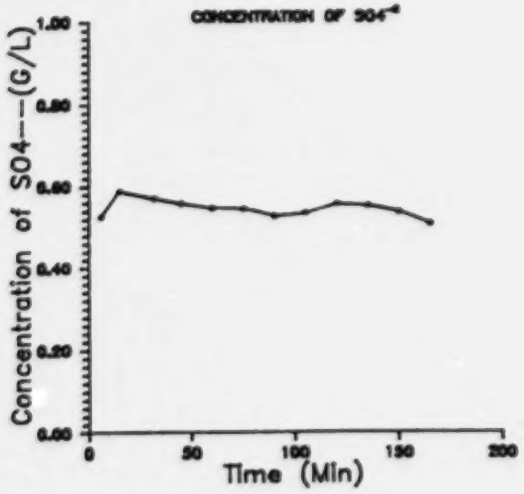
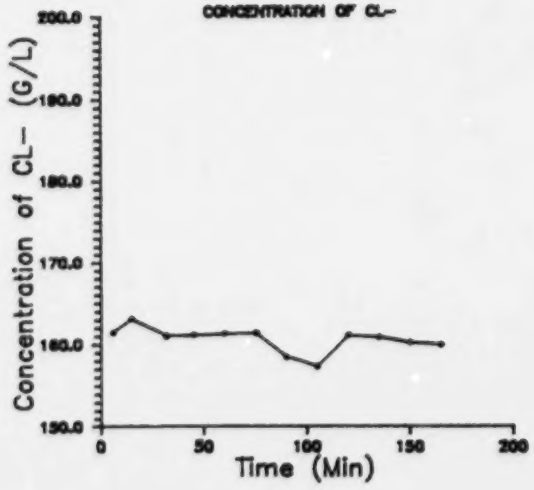


Figure 73 - Concentration of Different Ions in the Solution vs Time
(Core Sample P)









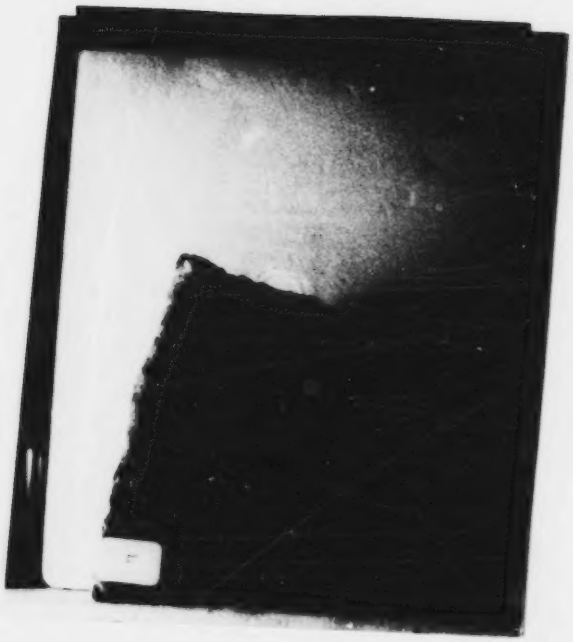


Figure 74 - Core Sample P - After Experiment

Figure 75 - Core Sample P - After Experiment

and plugs the flow of the fluid. To avoid the plugging, glycerol was added to the solution. Glycerol was added for the purpose of increasing the drag fore on the particle in the direction of flow (Appendix B). Glycerol postponed the plugging but could not stop it. The experiments could not be run for more than three hours.

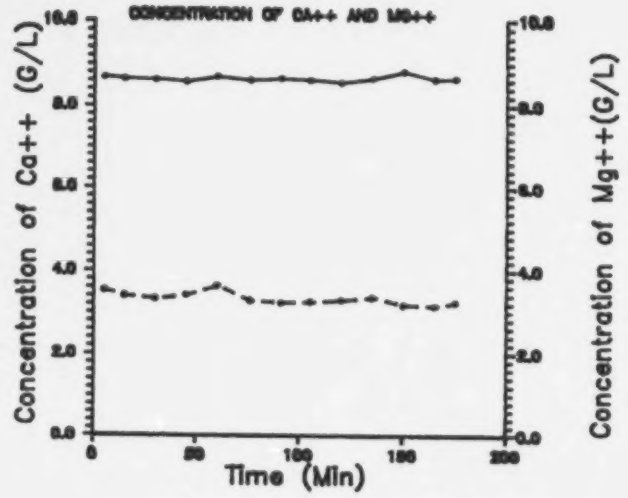
Three cores of T, Z and U were treated with brine + KCl. The amount of KCl added to the brine were 30 g/L and 20 g/L for two cores of T and U respectively. Core Z was treated with 100 grams of KCl and 150 mL of glycerol per litre of brine.

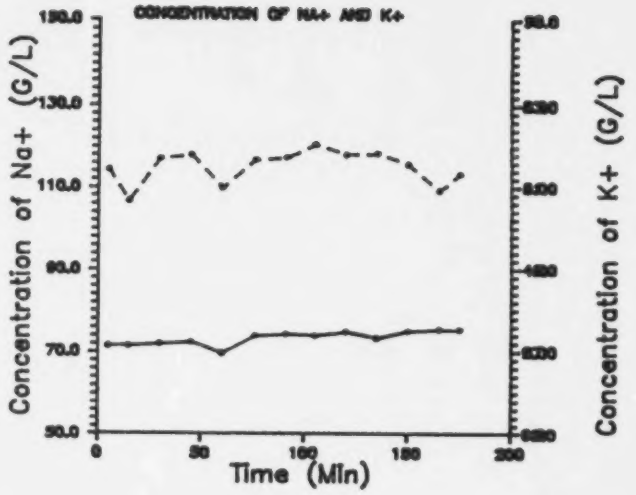
There was no significant dissolution observed in core Z because of the high amount of KCl added. Dissolution in cores U and T were higher because of the lower amount of KCl added to the brine. Figure 76 shows almost no changes in concentration of ions except in one point in Cl^- and K^+ concentration. This peak is because of the change in concentration of KCl that was added to the brine. The number of peaks are more in Figures 77 and 78 for cores U and T and are present for Na^+, K^+ and Cl^-. Any increase in K^+ concentration would cause a reduction in Na^+ concentration.

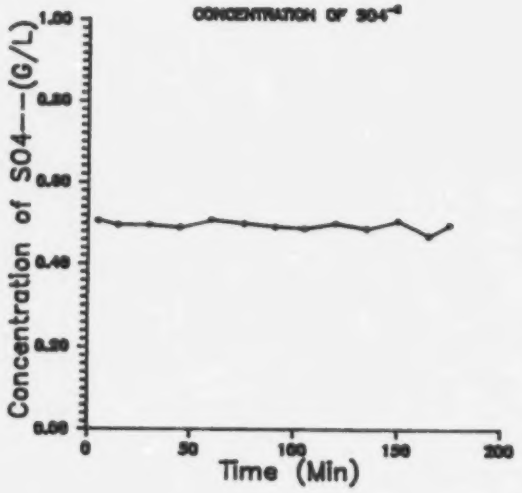
Brine + Na_2SO_4 as Suppressant

Na_2SO_4 was added to the brine as suppressant and the solution was pumped past a core. Precipitate formed in the solution and plugs the flow of fluid. Glycerol was added to the solution, to postpone the plugging process (Appendix B). Different amounts of Na_2SO_4 were added to the brine. Core samples of M, E and G were treated with 3, 3 and 5 gram of Na_2SO_4 per litre of brine respectively. Core samples of WZ, S, K and N were in contact with brine + 5 g/L Na_2SO_4 + 80 mL/L glycerol, brine + 5 g/L Na_2SO_4 + 80 mL/L glycerol, brine + 10 g/L Na_2SO_4 + 120 mL/L glycerol and brine + 2.5 g/L Na_2SO_4 + 40 mL/L glycerol.

Figure 76 - Concentration of Different Ions in the Solution vs Time
(Core Sample Z)







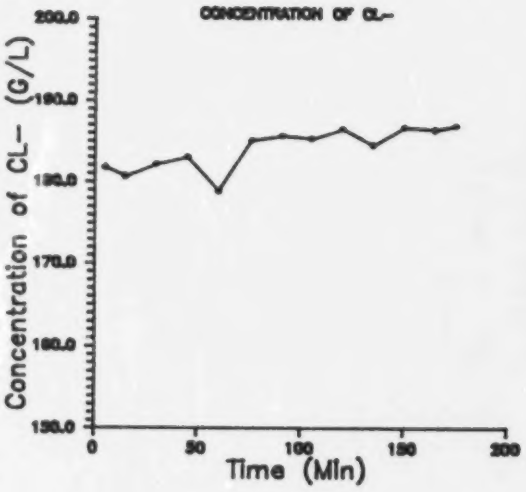
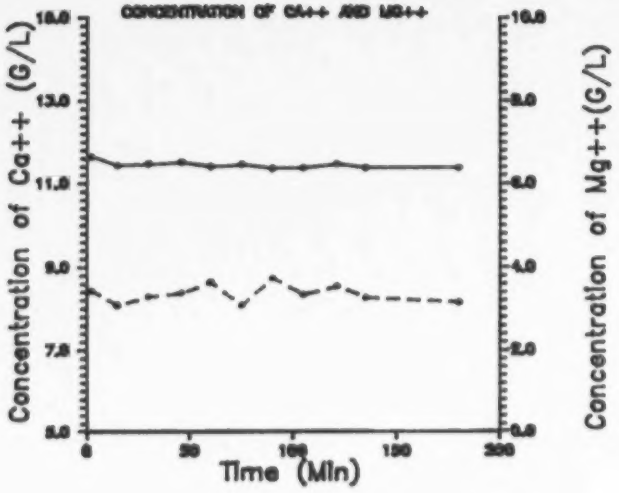
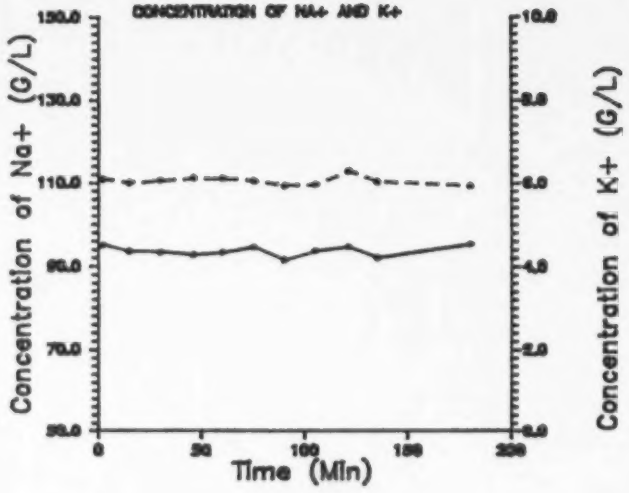
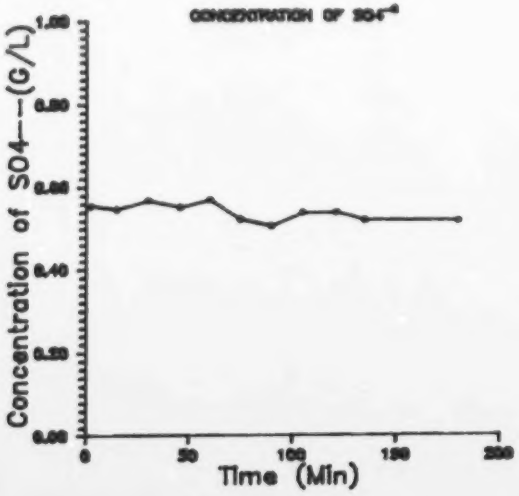


Figure 77 - Concentration of Different Ions in the Solution vs Time
(Core Sample U)







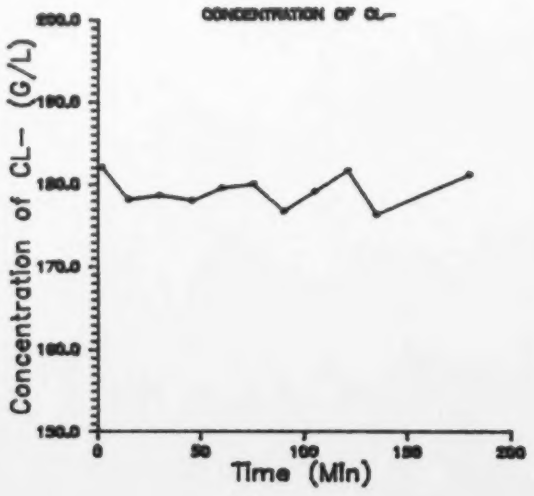
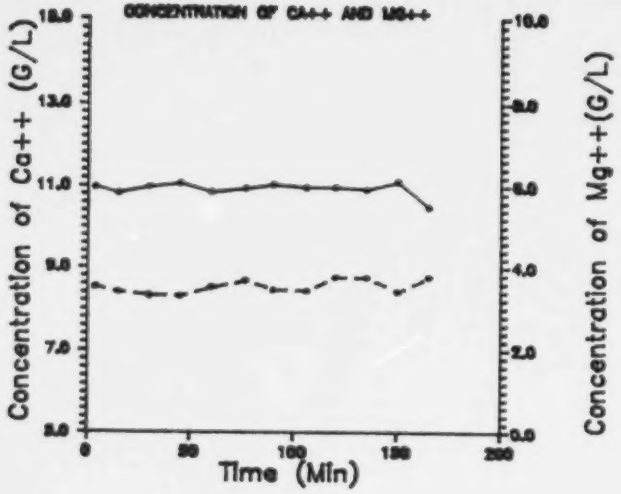
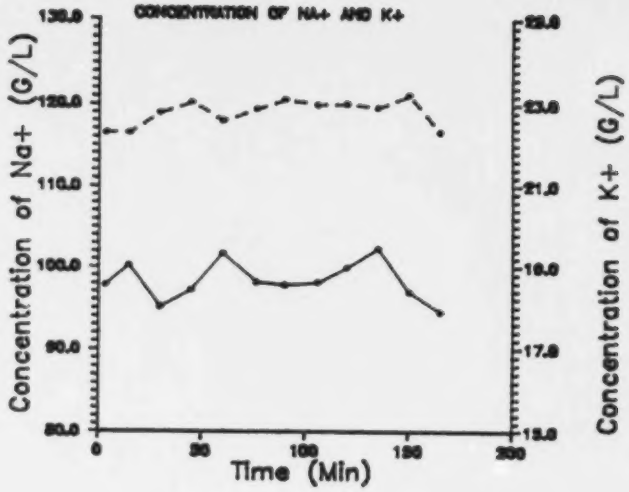
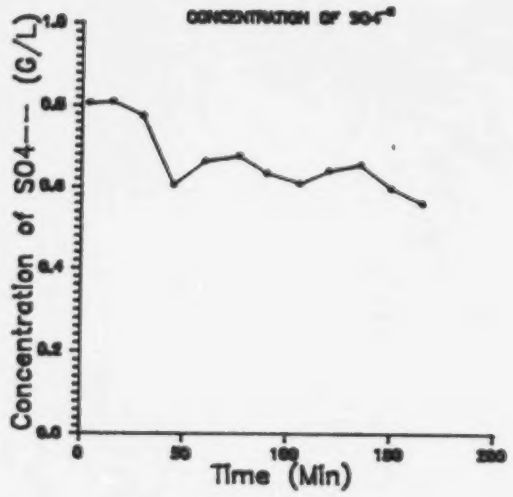
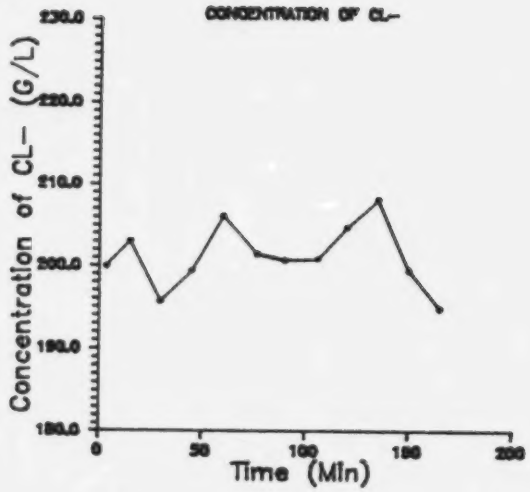


Figure 78 - Concentration of Different Ions in the Solution vs Time
(Core Sample T)









Results of sample G could not be replied upon because of the leakage that was observed after 5 minutes and continued throughout the process (Figure 79). Dissolution of particles from 3 cores of K, S and WZ were insignificant. For sample K, the experiment could continue for only 30 minutes because of the high amount of Na_2SO_4 (10g/L) and even 120 mL/L of glycerol was not effective. Higher amounts of glycerol may be required. Changes in concentration of ions occurred in Na^+, Cl^- and $SO_4^=$ ions and in less amounts in Ca^{++} (Figure 80). In WZ core, no dissolution occurred. Ion concentration changes are very small (Figure 81). Concentration of ions has few peaks in Cl^-, Na^+, Ca^{++} and $SO_4^=$, indicating the precipitation of $CaSO_4$ or NaCl (Figures 82, 83, 84 and 85).

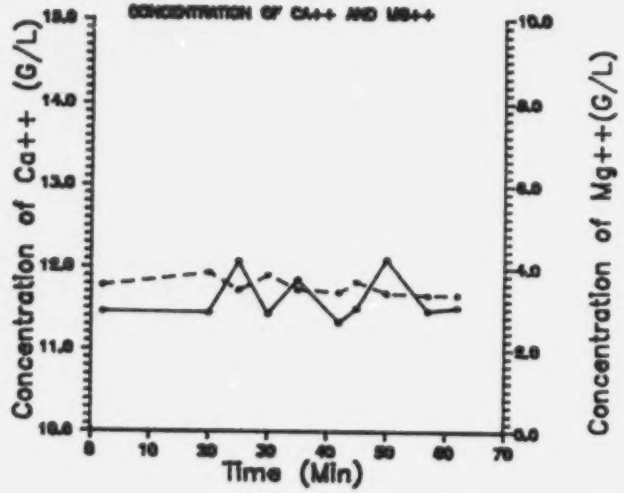
We could conclude that higher amounts of Na_2SO_4 could reduce the rate of dissolution even further. On the other hand it could cause the plugging of the flow. Hence, a balance between these two factors had to be considered. Figures 86, 87, 88, 89 and 90 show the picture of cores E, M, K, N and S after the experiment. Holes of 1 cm diameter were made in cores K and S to observe the formation of precipitates in these two cases.

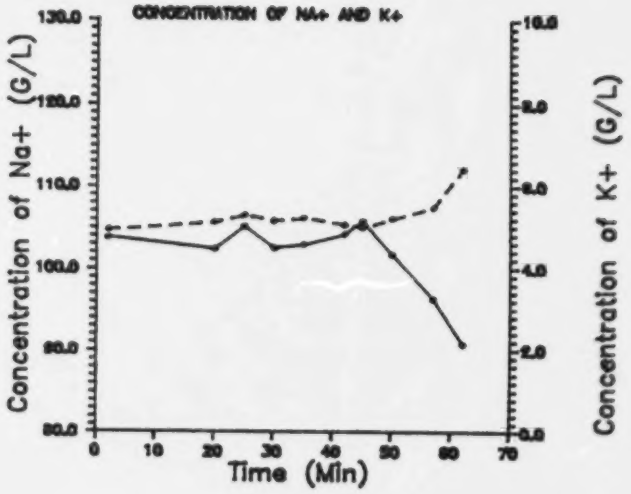
5.2 Mathematical Modelling Results

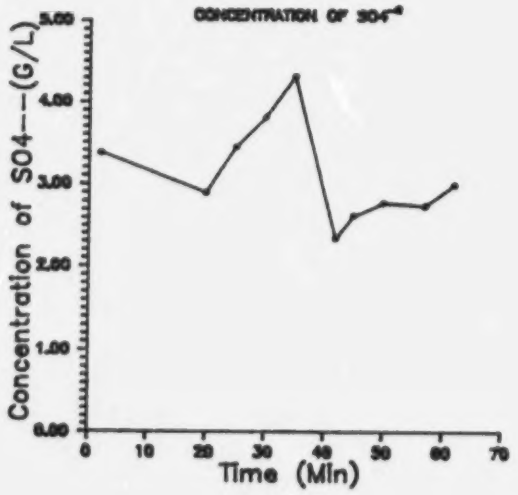
The Harvie and Weare[9] model at 25°C was tested with pure and complex experimental data. The required input data for this model are molality of the components in a mixture, CO_2 pressure, No. of iterations, alpha, frax and alpha 2. These last three factors determine the amount of each component that will be added or subtracted in each iteration and the amount of precipitate that could be fractionated.

The experimental results of Lee and Egerto[14] and Keitel[15] and Linke[16] for the system KCl - $MgCl_2$ - H_2O are tabulated in Table 41a. The theoretical results of the Harvie and Weare model are shown in Table 41b. Comparison of these two tables indicate that the model could predict the saturation concentrations in

Figure 79 - Concentration of Different Ions in the Solution vs Time
(Core Sample G)







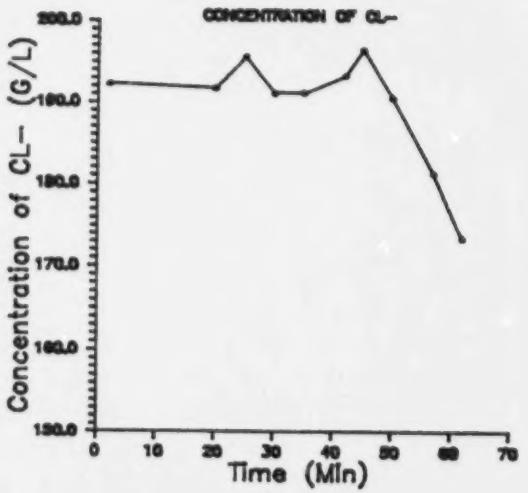
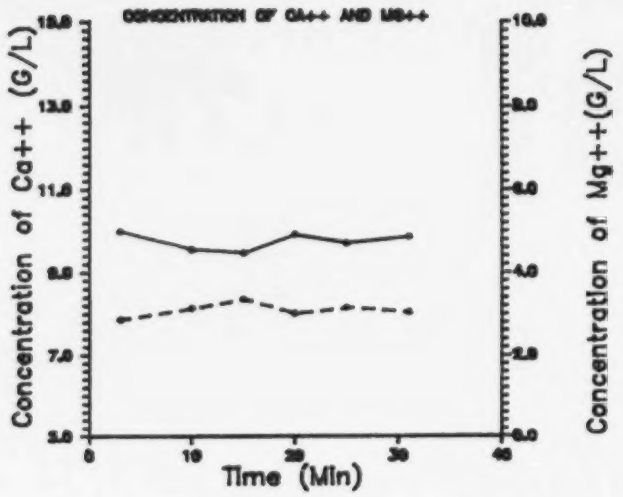
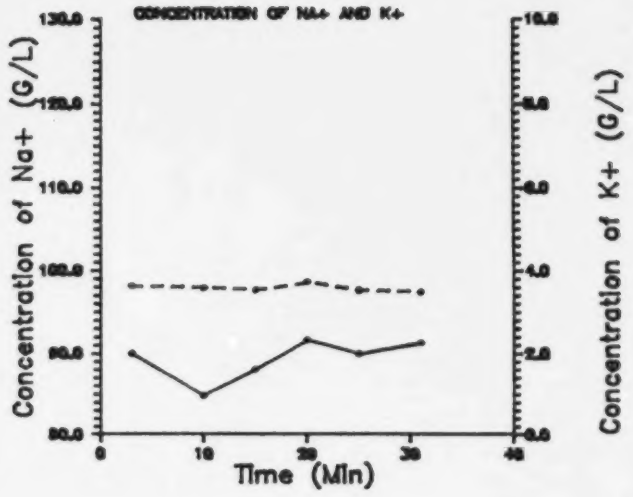
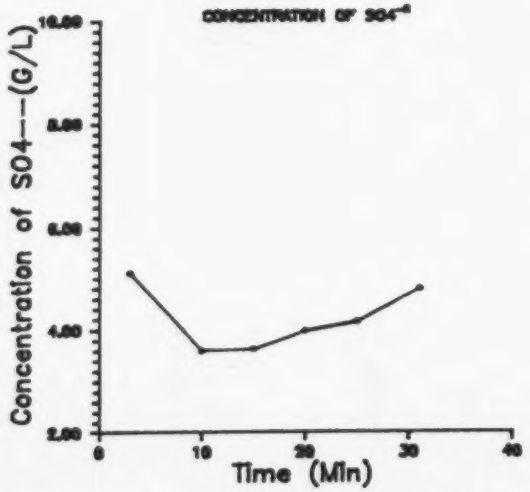


Figure 80 - Concentration of Different Ions in the Solution vs Time
(Core Sample K)







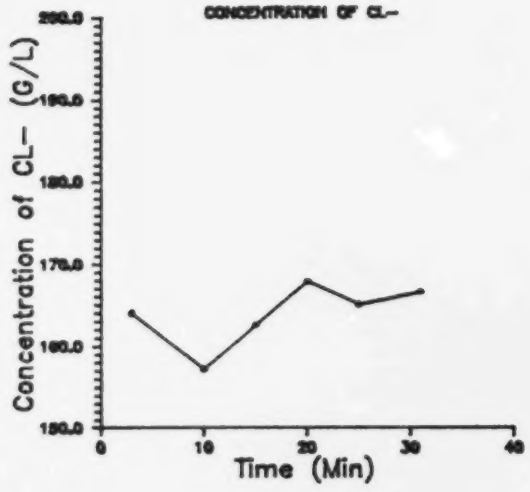
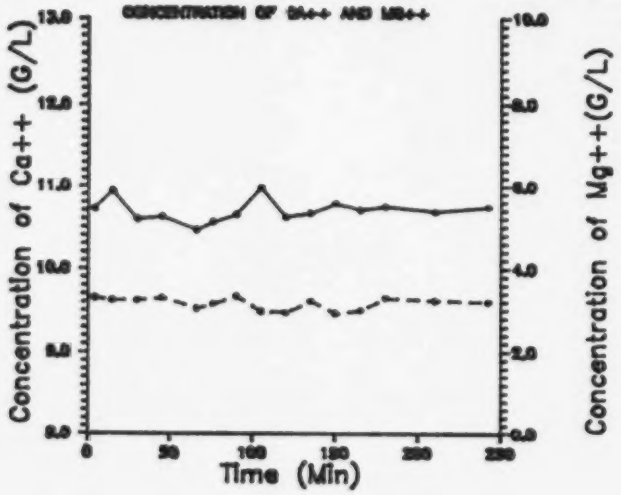
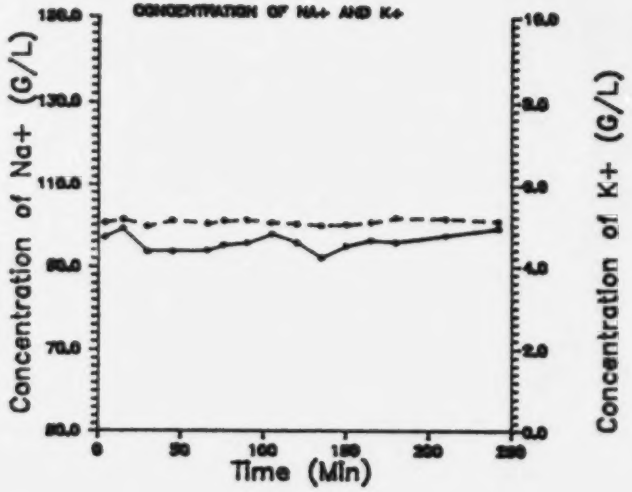
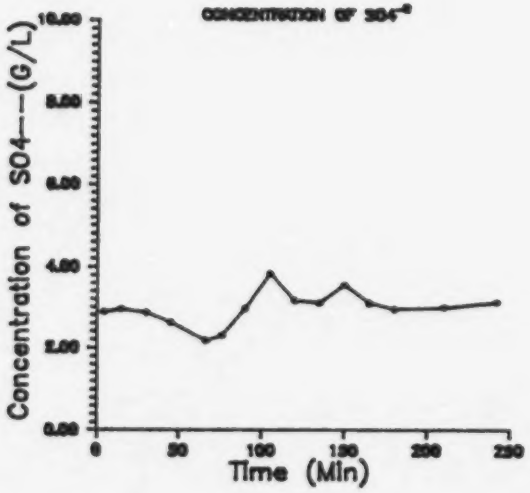


Figure 81 - Concentration of Different Ions in the Solution vs Time
(Core Sample WZ)







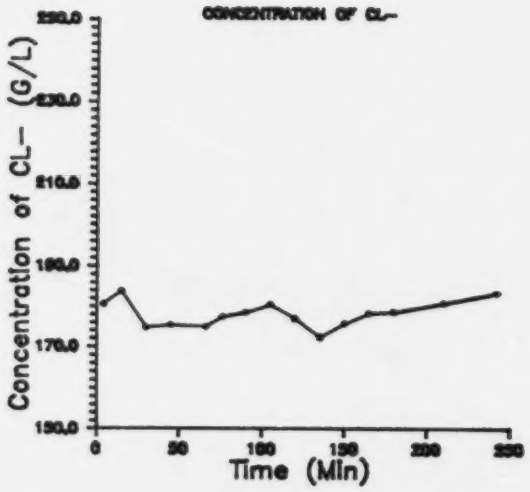
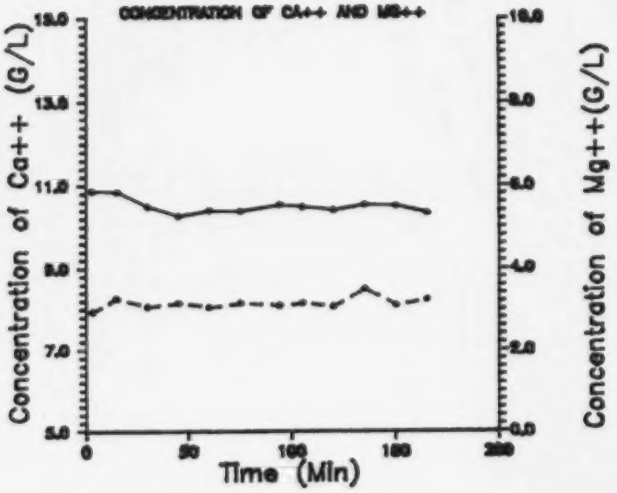
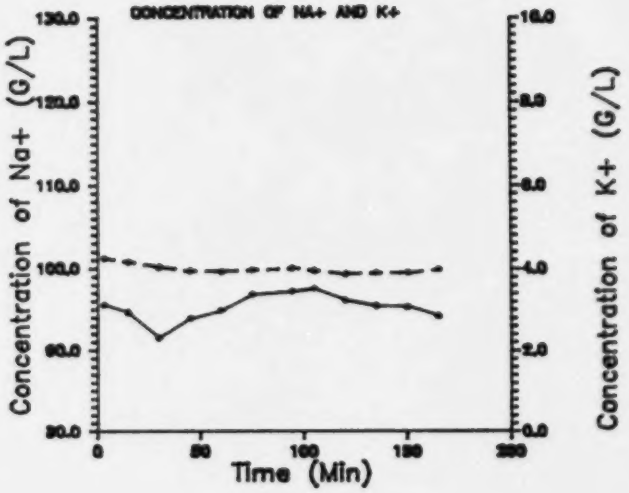
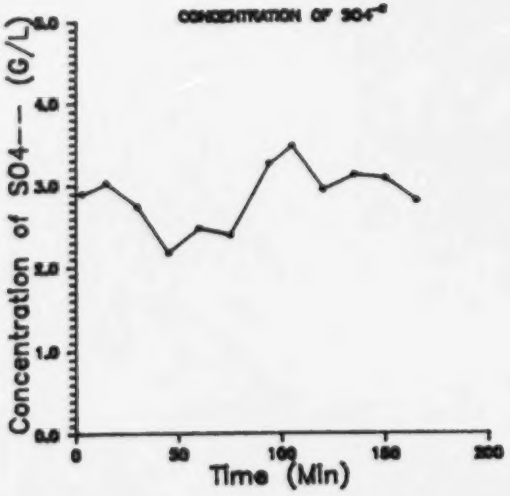


Figure 82 - Concentration of Different Ions in the Solution vs Time
(Core Sample S)







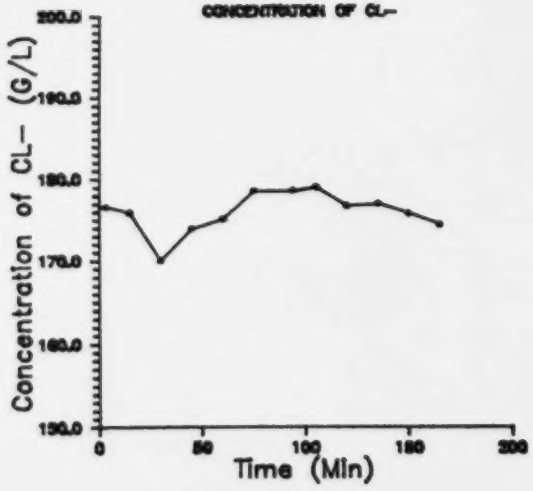
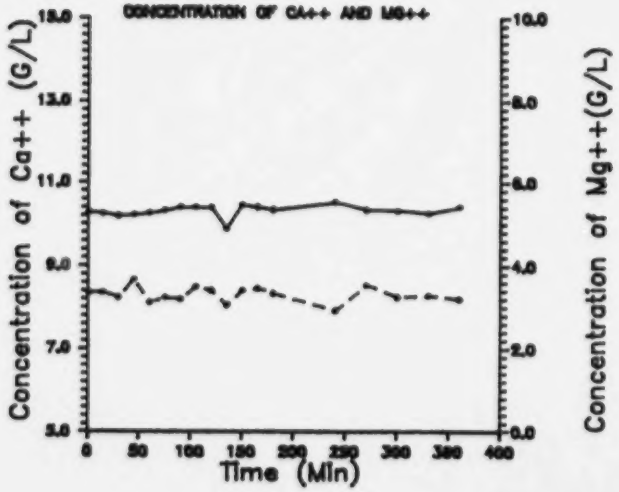
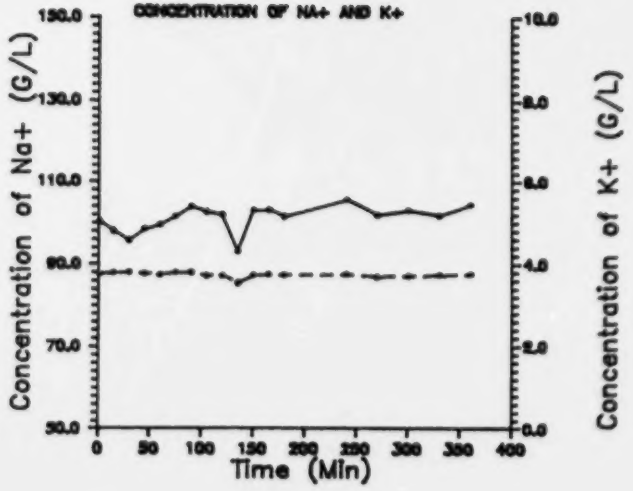
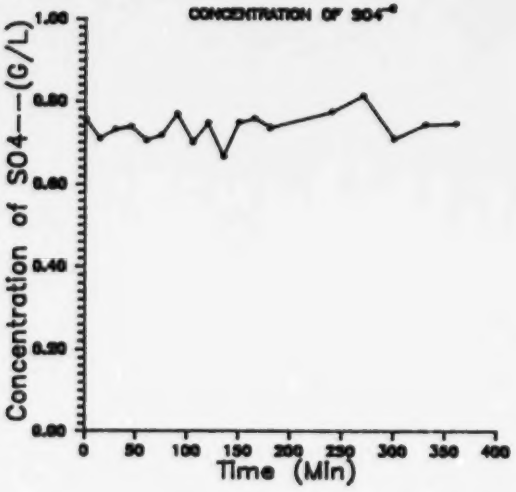


Figure 83 - Concentration of Different Ions in the Solution vs Time
(Core Sample N)







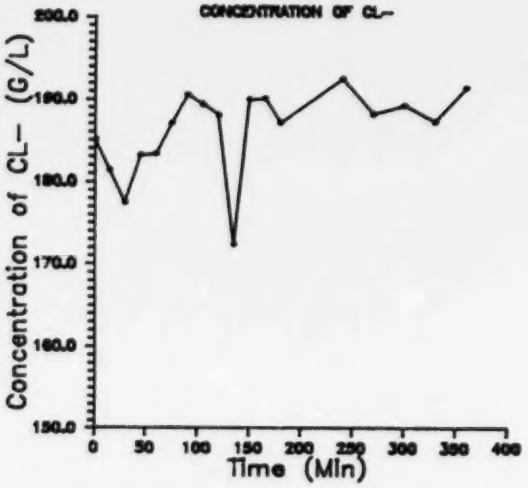
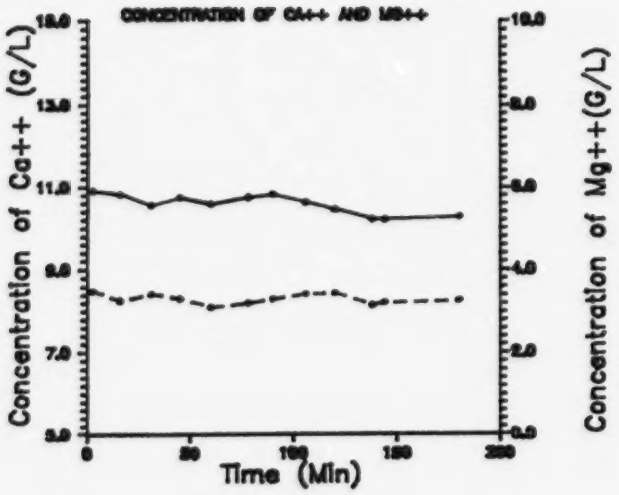
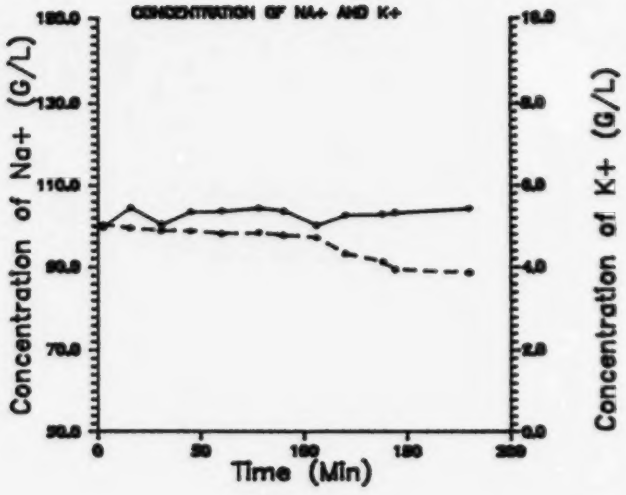
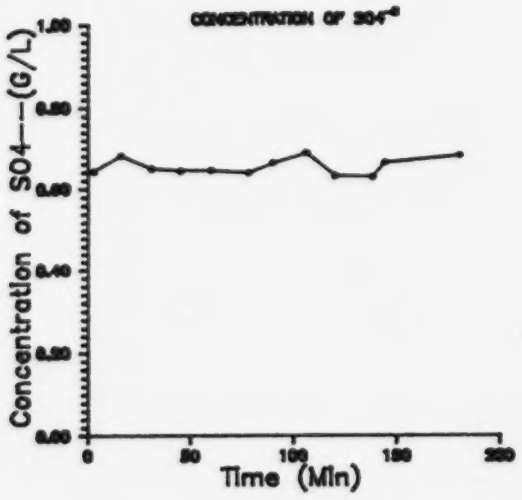


Figure 84 - Concentration of Different Ions in the Solution vs Time
(Core Sample M)







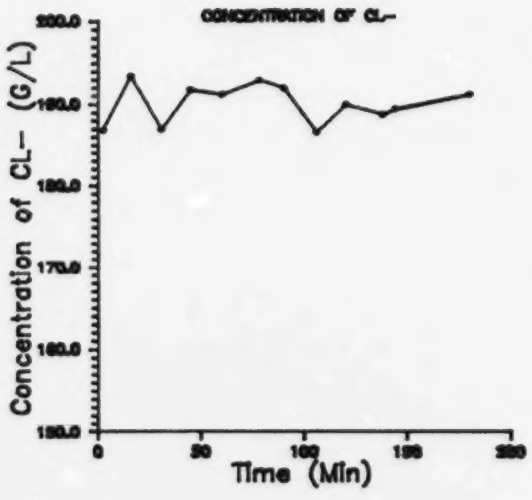
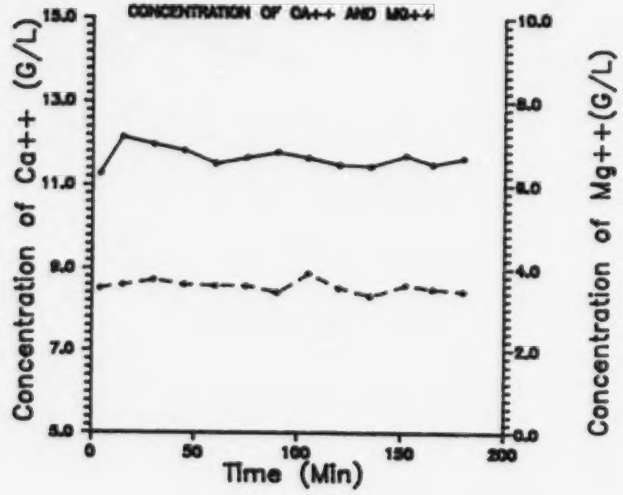
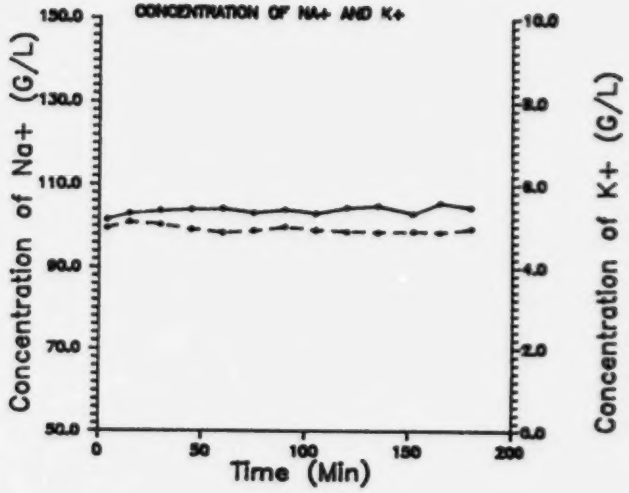
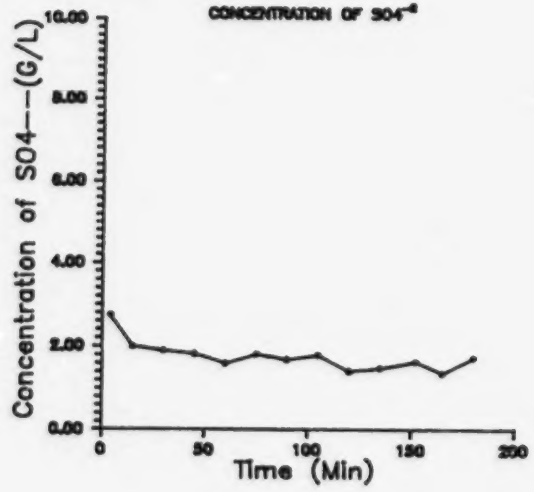


Figure 85 - Concentration of Different Ions in the Solution vs Time
(Core Sample E)







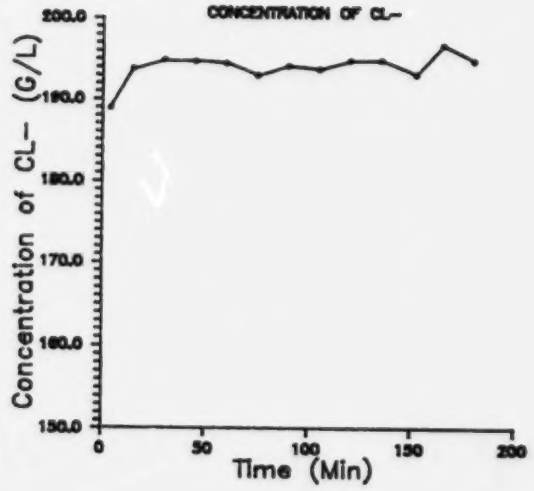


Figure 86 - Core Sample E After Experiment

Figure 87 - Core Sample [redacted] After Experiment

Figure 88 - Core Sample M After Experiment

Figure 89 - Core Sample N After Experiment

Figure 90 - Core Sample S After Experiment

ble 41- The System of $MgCl_2$ & KCl at 25°C

a-(Lee & Egerto, Keitel, 1923), Linke(1965)

Grams per 100g Sat. Solution		Molality (m)		Precipitate
KCl	$MgCl_2$	KCl	$MgCl_2$	
26.74	0.00	4.800	0.000	KCl
19.50	7.68	3.590	1.110	KCl
13.56	12.11	2.400	1.700	KCl
11.54	15.64	2.127	2.250	KCl
10.36	16.40	1.898	2.350	KCl
7.90	19.83	1.467	2.880	KCl
6.06	23.10	1.148	3.420	KCl
5.22	24.58	0.998	3.670	KCl
4.56	26.81	0.890	4.100	KCl
3.19	25.66	0.610	3.980	KCl
3.27	26.80	0.627	4.020	KCl+ Carnallite
3.70	27.70	0.724	4.156	KCl+ Carnallite
0.50	35.14	0.100	5.729	Carnallite+ $MgCl_2$
0.00	35.54	0.000	5.780	$MgCl_2$

b- (Harvie & Weare Model at 25°C)

Concentration (molality)		Precipitate
KCl	$MgCl_2$	
4.790	0.005	sylvite
4.030	0.500	sylvite
3.320	1.005	sylvite
2.650	1.505	sylvite
2.060	2.000	sylvite
1.566	2.505	sylvite
1.165	3.000	sylvite
0.856	3.505	sylvite
0.627	4.000	sylvite
0.370	4.240	Carnallite
0.147	4.525	Carnallite

a pure system very closely. Figure 90 also compares both the experimental data and theoretical results for this system.

The theoretical data for the system NaCl - Na_2SO_4 - H_2O is calculated from the Harvie and Weare model and shown in Table 42b. The experimental data of Seidell[17] and Linke[16] for this system is also shown in Table 42a. Comparison of these two set of data indicate the close prediction of these theoretical data with the experimental results (Figure 92).

The experimental and theoretical data for the system KCl - $CaCl_2$ - H_2O are shown in Tables 43 and 44 respectively. Figure 92 compares the results on a triangular diagram.

Similar comparison were carried out for the complex brine samples. Table 45a shows the concentration of different components in the CCP brine sample, CCP brine plus an equal volume of saturated $CaCl_2$ in water and CCP brine plus an equal volume of saturated Na_2SO_4 in water. Addition of the saturated solution of $CaCl_2$ and Na_2SO_4 to the CCP brine has caused the formation of precipitates in the solution. The kind of precipitate formed and its amount are shown in Table 45b. Our experimental results (Ref. 1) are also reported in the same table. This comparison indicates that the H & W model can predict the formation of precipitates in the complex brine sample very well. Similar calculations were performed on Cory Brine, IMC-K_2, Rocanville and Shaft Brine samples. Results are tabulated in Tables 46, 47, 48 and 49 respectively. Similarity of experimental[1] and theoretical results show the good prediction of the H & W model. Saturation solution of $CaCl_2$ in water contain 736 g/L of $CaCl_2$ and saturation solution of Na_2SO_4 contains 200 g/L of Na_2SO_4.

Figure 91 - THE SYSTEM MGCL2 AND KCL AT 25 C

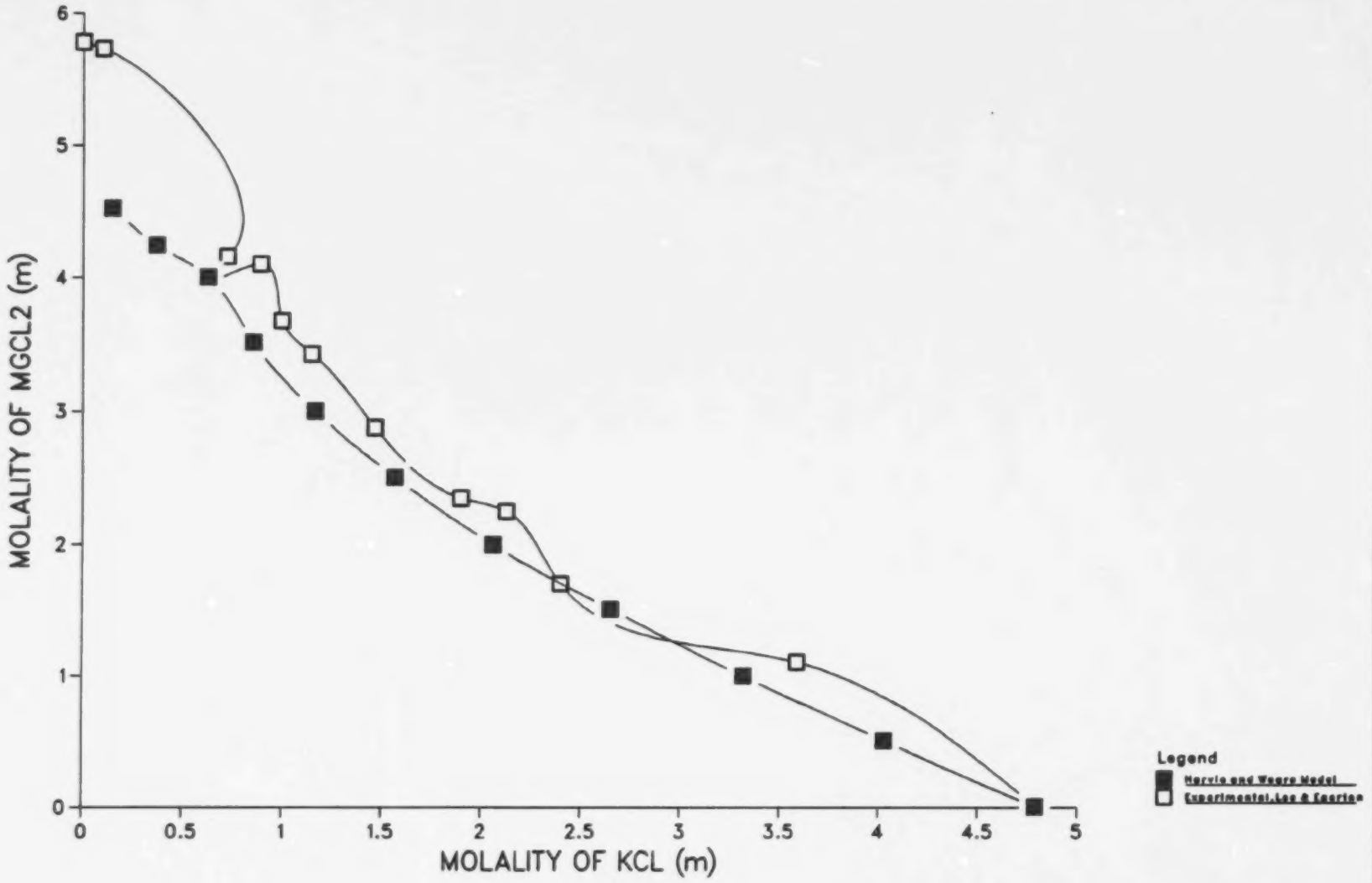


Table 42 - The System of $NaCl-Na_2SO_4-H_2O$

a. Results of Seidell,1902 at 25°C,Linke(1965)

Grams per 100g H_2O		*Molality (m)*		*Precipitate*
NaCl	Na_2SO_4	NaCl	Na_2SO_4	
2.96	26.60	0.51	1.82	$Na_2SO_4.10H_2O$ + Na_2SO_4
5.79	24.32	0.99	1.71	$Na_2SO_4.10H_2O$ + Na_2SO_4
9.90	21.41	1.69	1.50	$Na_2SO_4.10H_2O$ + Na_2SO_4
13.43	19.62	2.29	1.38	$Na_2SO_4.10H_2O$ + Na_2SO_4
15.82	19.64	2.70	1.40	$Na_2SO_4.10H_2O$ + Na_2SO_4
19.13	20.73	3.20	1.45	$Na_2SO_4.10H_2O$ + Na_2SO_4
23.22	16.28	3.97	1.15	Na_2SO_4 + NaCl
26.54	12.64	4.53	0.89	Na_2SO_4 + NaCl
31.06	9.98	5.30	0.70	Na_2SO_4 + NaCl
32.41	9.93	5.54	0.69	Na_2SO_4 + NaCl
33.00	9.84	5.64	0.69	Na_2SO_4 + NaCl
33.81	6.66	5.78	0.47	Na_2SO_4 + NaCl
34.60	3.38	5.91	0.23	Na_2SO_4 + NaCl
35.80	0.00	6.11	0.00	Na_2SO_4 + NaCl

b. Harvie & Weare Computer Model at 25°C

Molality (m)		*Precipitate*
NaCl	Na_2SO_4	
0.50	1.750	$Na_2SO_4.10H_2O$
1.00	1.550	$Na_2SO_4.10H_2O$
1.50	1.410	$Na_2SO_4.10H_2O$
2.00	1.330	$Na_2SO_4.10H_2O$
2.50	1.314	$Na_2SO_4.10H_2O$
3.00	1.314	$Na_2SO_4.10H_2O$
3.50	1.177	Na_2SO_4
4.00	0.973	Na_2SO_4
4.50	0.797	Na_2SO_4
4.99	0.648	Na_2SO_4 + NaCl
4.99	0.648	Na_2SO_4 + NaCl
4.99	0.648	Na_2SO_4 + NaCl

Figure 92 - SOLUBILITY OF NACL IN NA2SO4 SOLUTION

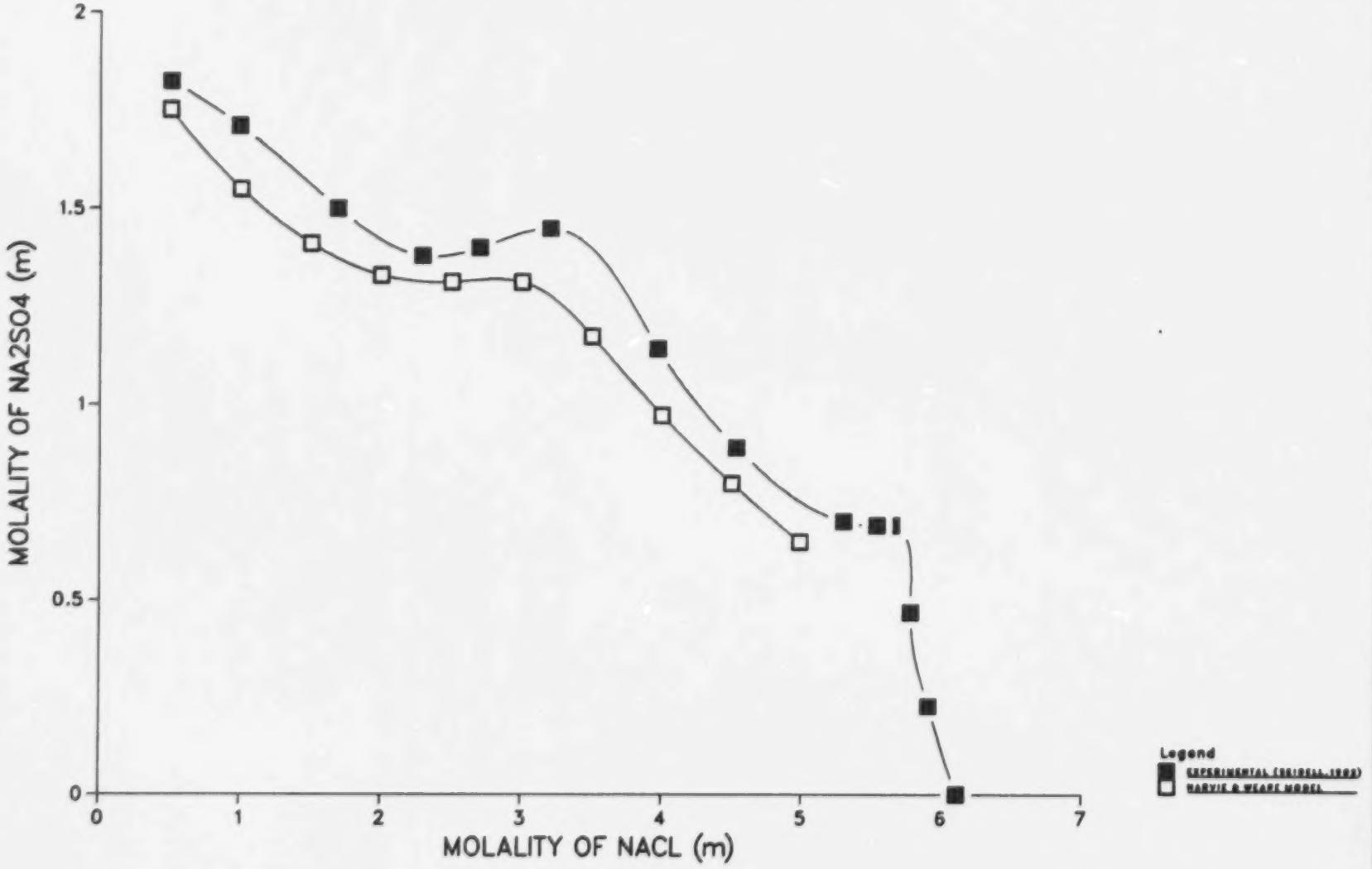


Table 43- The System KCl $CaCl_2$ H_2O at 25°C

(Data Linke (1958) & D'Ans (1933))

Reference	Grams per 100g Sat. Solution		Solid Phase
	KCl	$CaCl_2$	
D'Ans	11.60	16.50	Sylvite
D'Ans	7.50	23.15	Sylvite
D'Ans	3.70	32.35	Sylvite
D'Ans	3.10	37.82	Sylvite
Linke	3.10	44.70	Sylvite
Linke	13.90	6.70	Sylvite
	21.09	0.00	Sylvite

Table 44- The System KCl $CaCl_2$ H_2O at $25^{\circ}C$

(Harvie & Weare Model)

Molality (m)		Grams per 100g H_2O		Weight %		Precipitate
KCl	$CaCl_2$	KCl	$CaCl_2$	KCl	$CaCl_2$	
4.125	0.50	305.86	55.50	22.46	4.07	Sylvite
3.941	0.64	293.60	71.04	21.50	5.00	Sylvite
3.480	1.00	259.25	111.00	18.91	8.10	Sylvite
2.880	1.50	214.56	166.50	15.50	12.05	Sylvite
2.340	2.00	174.33	222.00	12.40	15.89	Sylvite
1.870	2.50	139.31	277.50	9.80	19.58	Sylvite
1.490	3.00	111.00	333.00	7.60	23.06	Sylvite
1.180	3.50	87.91	388.50	5.90	26.31	Sylvite
0.940	4.00	70.00	444.00	4.60	29.32	Sylvite
0.770	4.50	57.44	499.50	3.60	32.08	Sylvite
0.640	5.00	47.68	555.00	2.90	34.62	Sylvite
0.543	5.50	40.45	610.50	2.90	34.62	Sylvite
0.473	6.00	35.24	666.00	2.00	39.15	Sylvite
0.423	6.50	31.51	721.50	1.80	41.15	Sylvite
0.389	7.00	28.98	777.00	1.60	43.02	Sylvite
0.369	7.50	27.49	832.50	1.47	44.76	Sylvite

Fig. 93 The System
$KCl - CaCl_2 - H_2O$

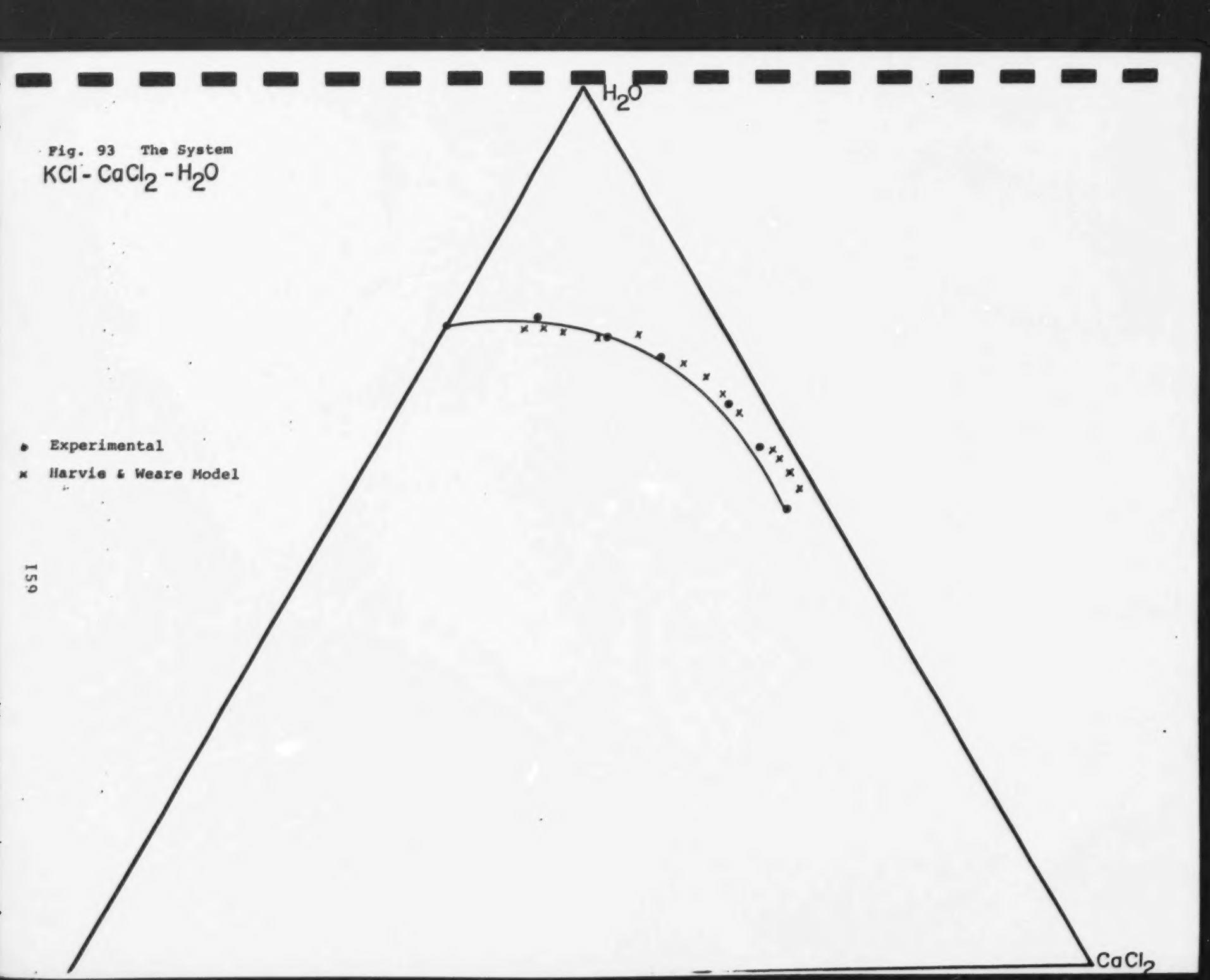


Table 45 - CCP Brine Samples

45a - Initial Concentration

Component	Concentration			
	Brine g/L	Brine Mole/L	Brine + $CaCl_2$ Mole/L	Brine + Na_2SO_4 Mole/L
Na^+	9.1520	3.979	1.989	3.389
K^+	3.798	0.097	0.048	0.048
Ca^{++}	11.726	0.293	3.461	0.146
Mg^{++}	4.092	0.165	0.083	0.080
Cl^-	176.930	4.980	9.120	2.490
$SO_4^=$	0.558	0.005	0.003	0.703
HCO_3^-	0.180	0.003	0.001	0.001

45b - H&W vs Experimental

Methods	Precipitates (Moles)		
	Brine	Brine + $CaCl_2$	Brine + Na_2SO_4
H&W Model	N.P.	Anhydrite (0.0024)	Gypsum (0.135)
Experimental	N.P.	Halite (0.467)	Gypsum (0.161)

Table 46: Cory Brine Samples

Components	Concentration (Mole/L)		
	Brine	Brine + CaCl2	Brine + Na2SO4
Na+	0.209	0.104	1.504
K+	0.390	0.195	0.195
Ca++	3.591	5.110	1.795
Mg++	0.888	0.444	0.444
Cl-	9.560	11.410	4.780
SO4--	0.002	0.001	7.010
HCO3-	0.000	0.000	0.000

Methods	Precipitates		
	Brine	Brine + CaCl2	Brine + Na2SO4
(H&W Model)	Anhydrite (0.002m)	Anhydrite (0.001m)	Gypsum (0.6975m)
(Experimental)	N.p.	N.P.	CaSO4

Table 47: IMC K2 Brine Samples

Components	Concentration (Mole/L)		
	Brine	Brine + CaCL2	Brine + Na2SO4
Na+	5.100	2.550	3.950
K+	0.128	0.060	0.035
Ca++	0.056	3.343	0.028
Mg++	0.047	0.024	0.024
Cl-	5.370	9.315	2.685
SO4--	0.0315	0.0158	0.7016
HCO3-	0.0009	0.0005	0.0005

Methods	Precipitates		
	Brine	Brine + CaCL2	Brine + Na2SO4
(H&W Model)	N.P.	Anhydrite + Halite	Gypsum
(Experimental)	N.P.	Halite	Gypsum

Table 48 - Rocanville Brine Samples

48a - Initial Concentration

Component	Concentration			
	Brine g/L	Brine Mole/L	Brine + $CaCl_2$ Mole/L	Brine + Na_2SO_4 Mole/L
Na^+	80.4	3.50	1.75	3.15
K^+	57.6	1.477	0.738	0.738
Ca^{++}	9.70	0.243	3.437	0.121
Mg^{++}	10.59	0.417	0.208	0.208
Cl^-	233	6.28	9.770	3.140
$SO_4^=$	0.878	0.009	0.0045	0.704
HCO_3^-	0	0	0	0

48b - H&W vs Experimental

Methods	Precipitates (Moles)		
	Brine	Brine + $CaCl_2$	Brine + Na_2SO_4
H&W Model	N.P.	Anhydrite (0.004) Halite (0.828)	Gypsum (0.0696) Syngenite (0.0408)
Experimental	N.P.	Halite	Gypsum

• Syngenite formula is $K_2Ca(SO_4)_2 \cdot 5H_2O$

Table 49 - Shaft Brine Samples

49a - Initial Concentration

Component	Concentration			
	Brine		Brine + $CaCl_2$	Brine + Na_2SO_4
	g/L	Mole/L	Mole/L	Mole/L
Na^+	106.68	4.640	2.32	3.72
K^+	20.31	0.520	0.26	0.26
Ca^{++}	7.014	0.175	0.402	0.087
Mg^{++}	3.290	0.130	0.062	0.06
Cl^-	204.20	5.750	9.510	2.87
$SO_4^=$	.0949	0.009	0.009	0.704
HCO_3^-	0.069	0.001	0.000	0.00

49b - Comparison of H&W and Experimental Result

Methods	Precipitates (Moles)		
	Brine	Brine + $CaCl_2$	Brine + Na_2SO_4
H&W Model	N.P.	Anhydrite (0.009) Halite (1.197)	Gypsum (0.077)
Experimental	N.P.	Halite	Gypsum

6. CONCLUSIONS

1. In the static tests, high amounts of suppressants could reduce the rate of dissolution of particles in the brine. The effectiveness of these suppressants in decreasing order are:

   20 gKCl > 30 g $CaCl_2$ > 125 mL methanol > 30 g Na_2SO_4

   These amount of suppressants were added to 150 mL of brine.

2. Among the suppressants tested, KCl is the only one that could possibly stop the dissolution of potash particles in brine (Figure 15).

3. The effect of low amounts of suppressant on the rate of dissolution at different temperatures can be quite negligible (Figures 35, 36, 37). High amounts of suppressant have the following order of effectiveness at different temperatures.

   KCl > $CaCl_2$ > Methanol > Na_2SO_4

4. The main resistance to reaction at different temperatures is the diffusion through the ash layer surrounding the particles and not the reaction step (low mixing rate).

5. At low speeds of mixing, dissolution of the particles is a gradual process in brine + suppressant solution. At higher speeds, however, it becomes like an instantaneous dissolution over a very short period of time (Figures 94 & 95). KCl is an exception (Figure 96).

6. At high mixing rates, the resistance due to diffusion through the ash layer is reduced and the rate of reaction becomes the controlling step.

7. The Kinetic study shows that the rate of reaction could be the controlling step in the dissolution of potash particles in brine alone (Figure 45). However, in the presence of suppressants any of the two steps of (1) diffusion through the ash layer or (2) rate of reaction could become the controlling step.

Figure 94 - *Kinetics of IMC Potash in Brine + Suppr*

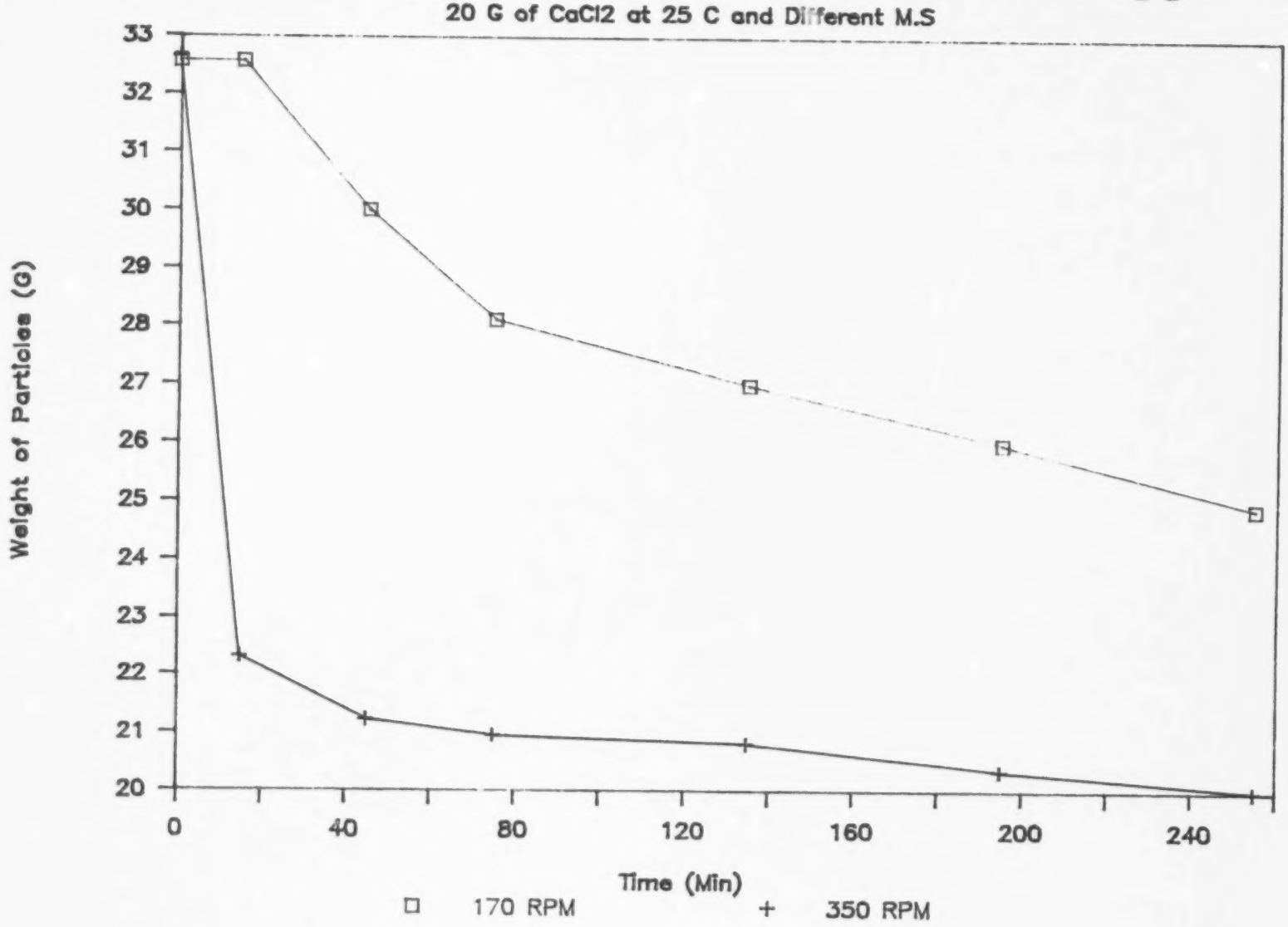


Figure 95 - *Kinetics of IMC Potash in Brine + Suppr*

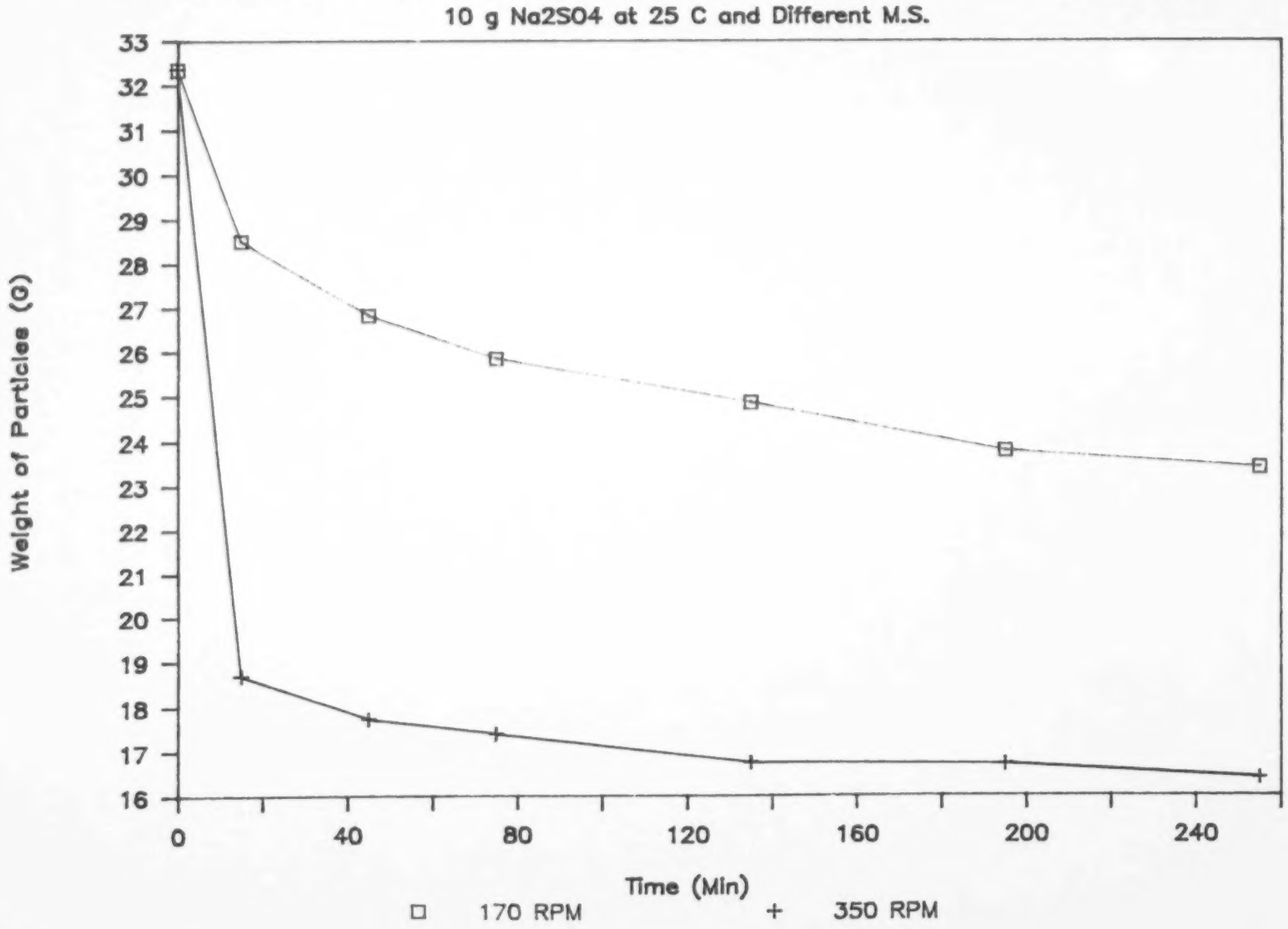
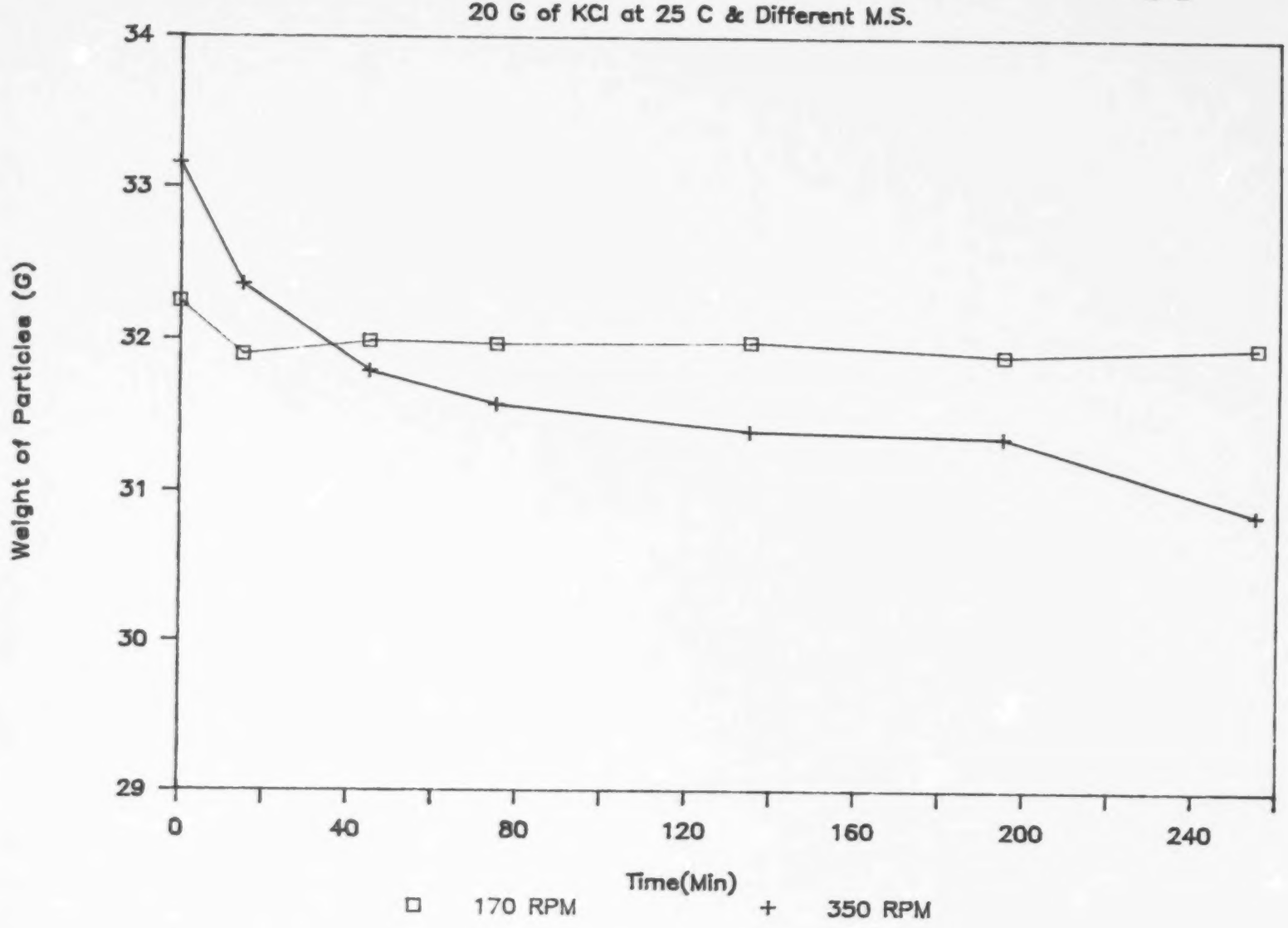


Figure 96 - *Kinetics of IMC Potash in Brine + Supp*



8. In the CSTR test, addition of suppressants could reduce the rate of dissolution of potash particles in the brine. It also helped by filling up holes that were artificially made in the potash core samples.

9. Plugging of the flow of fluid through the vessel could be postponed in some cases by the addition of glycerol to the brine solution (Appendix B).

10. KCl seems to be the best suppressant for reducing the rate of dissolution (CSTR Test). However, it also formed a precipitate and plugged the flow of fluid quickly (CSTR test).

11. $CaCl_2$ formed a colloidal solution in the brine and it did not produce any plugging problem in the vessel (CSTR test).

7. RECOMMENDATIONS

1. Assemble and test the Harvie & Weare extended computer model for high temperatures.

2. Carry out the plug flow test to determine the permeability characteristics and the effect of suppressant on permeability of potash cores.

8. ACKNOWLEDGEMENTS

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To - Appendices

Appendix A

Analytical Tests

The following tests were carried out on different samples for determination of the composition.

Compound	Test
KCl	Standard STPB Method
cl ion	Silver Nitrate Precipitation
Ca^{++} ion	Titration by EDTA
SO_4 ion	Addition of $BACl_2$ to form $BaSO_4$ precipitate
Bicarbonate	Titration with H_2SO_4
Density	Weight & Volume Measurement
Liquid Samples	By Philips 1480 X-Ray Fluorescence Xpectrometry

Appendix B

Drag Force on Immersed Objects

If V is the relative mean velocity of a fluid to a particle of projected cross-sectional area A, the drag force in the direction of V is calculated from an expression which defines the drag coefficient.

$$F_D = D_D \rho.V \text{ abs } V.A/2$$

C_D depends on the Reynolds Number dVp/μ, where d is a characteristic dimension of the object, C_D also depends on the shape and surface roughness. C_D also depends on the degree of turbulence and the acceleration of the fluid relative to the particle. For steady flow past spheres the relationship is as follows:

$$\begin{array}{lll} C_D = 24/Re_p & \text{if} & Re_p<1 \\ C_D = 24/Re_p\ (1 + 0.15\ Re_p^{0.687}) & & 1< Re_p<1000 \\ C_D = 0.44 & & 1000<Re_p,10^5 \end{array}$$

To increase the drag force on the particles (if velocity and density are constant), we had to increase the value of C_D. C_D is inversely proportional to Reynold No. for lower values of Rep and it is constant for higher values. Therefore,

$$F_D \propto \frac{1}{\frac{DV\rho}{\mu}} \cdot \rho f\ V_{abs}.V.A/2 \qquad \text{if } Re_p<1000$$

or

$$F_D \propto \mu$$

By increasing the viscosity of the fluid (μ), the drag force on the particle could be increased (if Re<1000). Additives such as glycerol were added to the brine in order to increase the viscosity and, hence, reduce the plugging rate.

For Re>1000, the drag force could be reduced only be increasing the velocity (V) or density of fluid (ρ). Viscosity has no effect on drag force.